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A TEXT-BOOK OF MODERN ORGANIC CHEMISTRY

FOR
B.Sc. CLASSES OF INDIAN UNIVERSITIES

by
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KHALSA COLLEGE, AMRITSAR

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*"A Text-book of Modern Inorganic Chemistry for B.Sc. Students";
"Introduction to Modern Physical Chemistry for B.Sc. Students";
"An Advanced Course of Chemical Calculations"; "Systematic
Organic Chemistry for Intermediate Students"; "Intermediate
Practical Chemistry"; "Elementary Chemical Calculations";
"Introduction to Organic Chemistry for Intermediate
Students"; "Elementary Organic Chemistry"; "Syste-
matic Inorganic Chemistry for Intermediate
Students"; etc., etc.*

WITH AN INTRODUCTION

by

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A TEXT-BOOK OF MODERN ORGANIC CHEMISTRY

INTRODUCTION

BY

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The scientific foundation of organic chemistry may be said to date from 1832 when Liebig and Wöhler published their classical investigation on the *Radical of Benzoic Acid*. The position of organic chemistry at that time may be understood from a letter written in 1837 by Wöhler to Berzelius in which he says: "It seems to me like the tropical forest, primeval, full of the strangest growths, an endless and pathless thicket, in which a man may well dread to wander." It is not implied that before this time no organic compounds were known. In fact, as early as the second half of the 17th century, chemical substances had been classified according to their origin from "the three kingdoms of Nature" by Nicolas Lemery in the famous *Cours de Chymie* (1675) under the following three divisions:

- (1) *Mineral substances*—such as metals, minerals, earth and stones.
- (2) *Vegetable substances*—such as plants, resins, gums, fruits, juices and honey.
- (3) *Animal substances*—Such as various parts of the animal body and excrements.

This is, thus, the first attempt to separate organic from inorganic chemistry.

The exact composition of chemical substances was not known at that time, although Stahl (1660—1734) pointed out the preponderance of what he called the "aqueous and combustible principles" (hydrogen and carbon) in substances of vegetable and animal origin. Scheele (1742—86) had isolated and studied many of the commoner organic acids and had discovered glycerine (1779) obtained by heating olive oil with litharge. Rouelle (1703—70) had discovered, among other substances, urea and hippuric acid. Many other organic products had

been discovered, but no real advance was possible until the foundation of *Atomic Theory* by Dalton (about 1803). Berzelius (1779—1848), the great Swedish chemist, whose classical work on the atomic weights of elements must always rank high for its accuracy, greatly improved the methods of organic analysis, *i.e.*, the methods for the determination of carbon, hydrogen, and nitrogen in organic substances. He further proved by his accurate analysis, especially of the salts of organic acids, that both in their composition and in the products of their decomposition, these substances followed the same fundamental laws of chemical combination as held for inorganic substances. This development was continued by Liebig who in 1831 introduced and improved adequate methods of organic analysis. Organic chemistry thus began to assume the status of an exact science. Organic compounds, like inorganic substances, could also be represented by means of molecular formulæ. This development was also largely due to Lavoisier (1743—94) who undertook the study of the composition of chemical substances. He found that most of the vegetable substances were built up of carbon, hydrogen and oxygen, and that these three elements, generally accompanied by nitrogen and sometimes by phosphorus and sulphur, were present in all substances of animal origin. He proved by direct experiment that organic substances had definite composition, and thus, recognized the fact that the general laws of chemical combination were equally applicable to all substances, irrespective of their origin or the degree of their complexity. In spite of the above-mentioned similarity found in organic and inorganic compounds, a sharp line of demarcation was drawn between the two groups, as regards their synthesis, by Berzelius and others. They pointed out that whereas inorganic substances could be synthesized from their constituent elements in the laboratory, this was not possible for organic compounds. It was imagined that a mysterious force of Nature was required for the synthesis of organic products and that it was beyond the power of the chemist to call this vital force into play. There was ample reason, too, at the time for this belief, based on the fact that such products had not so far been synthesized in the laboratory. The real reason for this failure to achieve the artificial production of such substances lay both in the complexity of organic products and the rudimentary state of synthetic chemistry at that time. As a result of this, the idea of a vital force remained for many years the barrier between organic and inorganic chemistry. Wöhler's synthesis of urea from ammonium cyanate and Hennel's preparation of alcohol from ethylene, both effected in 1828 in the laboratory, shook the belief in the vital force theory. An ever-growing number of organic syntheses of plant products, such as alizarin and indigo, as well as of many products of animal change,

such as uric acid, gave a death-blow to the "Vital Theory of Berzelius."*

As a result of the improvements effected in organic analysis by Berzelius, and more especially by Liebig (1831), it was established by Lavoisier and others that organic compounds were composed of carbon combined with about half a dozen other elements, of which hydrogen, oxygen and nitrogen were predominant. In this respect, these organic compounds stand in marked contrast to inorganic compounds. It is unusual to find more than three or four inorganic compounds built up from the same three elements, whereas a practically unlimited number of organic compounds may be derived from carbon, hydrogen and oxygen. This is due to the remarkable capacity of carbon for combining with itself. Thus, compounds are known in which as many as sixty carbon atoms are directly united to each other. Though the distinction between organic and inorganic chemistry based on the vital force theory has disappeared, the vast number of known organic compounds—now well over 250,000—which exceeds that of the compounds of all the other elements put together, is a strong argument for treating organic chemistry as a distinct and separate branch of chemistry. The reason is, therefore, purely one of convenience. "Organic Chemistry" is, therefore, best defined as the "Chemistry of the Carbon Compounds", as the element carbon is the invariable constituent of these compounds.

The second point which distinguishes organic from inorganic chemistry is the phenomenon of Isomerism, which is so common in the former. Wöhler's discovery was also important in another way: the doctrine of isomerism was its direct outcome. Wöhler sought to prepare the ammonium salt of cyanic acid; instead he obtained the highly stable substance, urea: the salt which was first formed in solution passed rapidly over into urea. The elementary composition and molecular formula of the two compounds is the same but they differ in structure: compounds so related are termed *isomeric compounds* or *isomers*, and the phenomenon is known as *isomerism* (Berzelius, 1831). Liebig and Wöhler had previously

*Nevertheless the "Vital Force" theory was right in one sense: There are many plant and animal products, such as, for instance, proteins, which we are unable to produce artificially. It must be admitted also that we are unable to reproduce Nature's methods and that our methods compared with hers, are clumsy and uneconomical. It is, however, certain, that in the not far distant future Biochemistry, which may be defined as the chemistry of life, may develop to the same degree of perfection as synthetic organic chemistry. When this is the case, we shall be able to imitate Nature as we can now do, in some cases, by employing her tools, as, for example, in the conversion of a sugar into alcohol by means of an enzyme.

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shown (1823) that silver cyanate and silver fulminate were similarly related. Camphor has, at least, 119 known isomers, each containing 70·9 per cent of carbon, 10·5 per cent of hydrogen and 10·5 per cent of oxygen. The molecular formula of these 120 distinct substances is the same, namely $C_{10}H_{16}O$, but the molecular structure and properties are different in each case. The recognition of the principle of isomerism was a great advance in chemical thought and it ultimately led chemists to depict the structure of the isomeric substances as a variable arrangement of the atoms in the molecular edifice. To use an analogy, suppose a wall to be built of ten black bricks, sixteen red bricks and one white brick, representing the three elements carbon, hydrogen and oxygen respectively. The organic chemist has so far discovered examples of 120 different ways in which these twenty-seven bricks can be arranged. It may be possible to arrange them in other ways, but at least he has the means of distinguishing these 120 different patterns. It is, however, different with most inorganic compounds. One has to be content with a knowledge of their composition only, in other words, with the nature and relative number of the atoms present. Sulphuric acid is represented by the formula H_2SO_4 and that formula represents no other substance.

Thirdly, organic or carbon compounds as compared with the compounds of other elements are unstable, and are generally decomposed at high temperatures. This has necessitated the development of special methods and processes of their investigation.

Lastly, organic compounds are much more complex than inorganic compounds; cane sugar is represented by the formula $C_{12}H_{22}O_{11}$, and stearin, one of the constituents of mutton fat and lard, by the formula $C_{57}H_{110}O_{68}$ and the molecules of starch or cellulose may number its component atoms in several thousands; whereas it is very seldom that the molecular formula of an inorganic substance contains more than a dozen atoms. These considerations clearly show that the treatment of carbon compounds as a separate branch called "Organic Chemistry" is not based on any fundamental difference between the two branches of chemistry. It is the result of recognition of the principle of the division of labour and is guided largely by considerations of convenience of the workers in the two fields.

The extraordinary development of organic chemistry which has been mentioned in the previous section is due to two main influences. One is the study of the structure of organic compounds which received a great impetus from the laws of Kekulé formulated in 1858. These laws are capable not only of co-ordinating and explaining a vast array of known facts included in organic chemistry, but also of predicting new ones with the result that

Organic
Chemistry
in Service
of Chemical
Industry.

organic chemistry has become almost the most exact of the sciences. If it were alone for these considerations, its development would not have been so great as what we find it to-day. The most important influence which has contributed largely in this direction is, however, of economical and technological interest. It was the application of the knowledge of organic chemistry to industry which has had a far-reaching effect in promoting the rapid growth of the science. The large profits which were made by the manufacturer were partly devoted to the advancement of research in technological laboratories and universities. This resulted in the rapid growth of chemical theory, which, in turn, reacted on chemical industry. A notable example of successful industrial research is the manufacture of indigo. In 1880, Von Baeyer accomplished the synthesis of indigo in the laboratory. This was taken up by the German dye-stuff industry, which, after seventeen years' strenuous labour and the expenditure of nearly £1,000,000, succeeded in establishing the synthesis on a large scale. The high and uniform purity of the synthetic product, coupled with its low price, resulted in the virtual extinction of the indigo-growing industry with dire loss to the European planters of Bihar, and consequent gain to the far-sighted German entrepreneurs who had the initiative and the ability to convert a laboratory experiment into a vast industry.

The position of the drug and medicinal chemical industry has been greatly improved by the introduction of synthetic compounds of therapeutic value, such as, aspirin, phenacetin, salol, sulphonal, medinal, antipyrine, salvarsan, saccharin and a number of others. Their manufacture is chiefly carried out by German dye-stuff industry as an adjunct to the preparation of dyes. As a result of the study of physiological action of synthetically prepared organic compounds, certain typical groups have been recognized as possessing specific narcotic, antiseptic, or antipyretic actions. Many natural products have been investigated from this point of view, and in many instance as, for example, in the case of the drug cocaine (present in coca leaves), the determination of structure has revealed the particular arrangement of atoms in the molecule, on which the physiological properties of the drug depend. Among the several synthetical products embodying this principle, which were prepared in the laboratory, the simpler novocaine, in the exercise of its particular medicinal functions, has been found more beneficial than the natural material cocaine.

The effect of the application of organic chemistry to industry is, perhaps, best seen in the introduction of synthetic colouring matters. No doubt the art of the dyer was thoroughly known to the ancient civilizations of which we have any knowledge; the ancient Egyptians and others were acquainted with the use of mordants and were able

to obtain fast shades of colour which have remained permanent for many centuries. But it must be admitted that the number of natural dyes was limited and even as late as the early part of the second half of the nineteenth century indigo, alizarin, extracts of logwood and other woods, safflower, cochineal among the natural dye-stuffs were the chief mainstay of the dyer. The earliest known artificial dye is picric acid, which was obtained from indigo in 1771. It is extensively used as a yellow dye for silk and wool and as a high explosive. In medicine it finds application as an antiseptic and is extensively used as a lotion for burns. The history of modern or synthetic dyes, however, commenced in 1856, when Perkin, at the early age of seventeen, prepared the first aniline dye, Mauve. It was a purely accidental discovery, but Perkin set up a factory at Greenford Green, near London, for its manufacture in the following year. A new era in dyestuff chemistry commenced and in less than eighty years thousands of new dyes were synthesized from coal-tar and hundreds of them have found useful application in other industries, such as textiles, leather, paper, paints, ink, etc. The dye-industry is intimately connected with the manufacture of explosives, as the primary and intermediate products are the same in the two cases. It is thus a "key industry" and this fact brought home vividly to the British Government during the last Great War when the supplies of these products were cut off. In 1913, Germany produced coal-tar dyes of the value of about £20,000,000 representing about three-fourths of the world's production. Although the coal-tar dye industry originated in England with the discovery of Perkin, it did not flourish in that country. The causes of its failure in England were two: firstly, the neglect of organic chemistry in the universities prior to 1880 by which time a large part of the business of manufacturing colours from coal-tar had already passed into the very competent hands of the Germans; and, secondly, the British manufacturer's disregard of the application of scientific and research methods to industrial processes.

Similarly, Sabatier's discovery that unsaturated organic compounds which are ordinarily indifferent to gaseous hydrogen could be successfully made to take up hydrogen with the aid of certain catalysts has had far-reaching effect in the technical practice known as the "hardening of fats and oils."

Although we are as yet far from synthesizing proteins, starches and celluloses, organic chemistry has been widely applied in the different cellulose industries. The textiles, artificial silks, paper-making, films, plastics, etc., require the help of the chemist. The "process and product control" enables the manufacturer to turn out a uniform and high quality product.

Natural petroleum, which is a complex mixture of hydrocarbons, has been known from very early times, and the "eternal fires of Baku" were known to fire-worshippers as early as 600 B.C. The economic exploitation and development of the petroleum industry, however, commenced after Kekulé had placed organic chemistry, on a scientific basis in 1858. When these natural resources are exhausted, as they must certainly be, in a few decades, services of organic chemistry will be required in producing cheap power alcohol or some other substitute for motive power. The enumeration of the services which organic chemistry has rendered or will render in future to industry is not exhausted, but enough has been said to show its tremendous value.

PART I
ORGANIC ANALYSIS AND GENERAL
THEORY
CHAPTER I

METHODS OF PURIFICATION AND CRITERIA OF PURITY

1. Purification of Organic Substances. The various methods employed for purifying organic substances are given below :

(1) **Crystallization.** The method of purifying an organic substance by crystallization is essentially the same as that employed for inorganic compounds, except that solvents such as alcohol, ether, light petroleum, chloroform, benzene, etc., are employed in addition to water. A hot, nearly saturated solution of the substance in a suitable solvent is first prepared. Any insoluble matter that may be present is filtered off, and the clear, hot solution allowed to cool ; crystals of the substance separate out, while the impurities are left behind in the mother liquor. The details of the procedure are :—

(i) *Preparation of Solution.* The first thing to do in this connection is the selection of the right solvent. Small amounts (a few milligrams will suffice) of the substance are put into a number of small test tubes, and treated with a small quantity of each of the common solvents. If the substance dissolves immediately in the cold, or if practically no dissolution occurs on warming, the solvent under trial is unsuitable. The suitable solvent will be that in which the substance dissolves on heating and from which it readily crystallizes out on cooling.

Having made a selection of the solvent, we must next determine the amount of it to be used. It should be just sufficient to make the solution, when hot, nearly saturated. Too large an excess of the solvent should be avoided, otherwise no crystals will form on cooling.

It should be remembered that the substance to be purified often contains insoluble impurities, and no attempt must be made to bring these into solution by the addition of a large amount of the solvent.

A suitable quantity of the well-powdered substance, along with the necessary amount of the solvent, is placed in a flask. If dissolution occurs readily, the flask is gently warmed on a water bath. Should it, however, be too slow, the flask is fitted with a reflux condenser and heated on the water or sand-bath (Fig. 1). This arrangement prevents the loss of the solvent by evaporation during the process of solution, and also the vapour of the solvent, if inflammable, from catching fire.

(ii) *Filtering the Hot Solution.* If the quantity of the solution is small, it may be filtered through an ordinary filter paper placed in a glass funnel with a short stem or a fluted filter fitted in a fluted funnel. In either case the funnel and the filter paper must be warmed just before filtering.

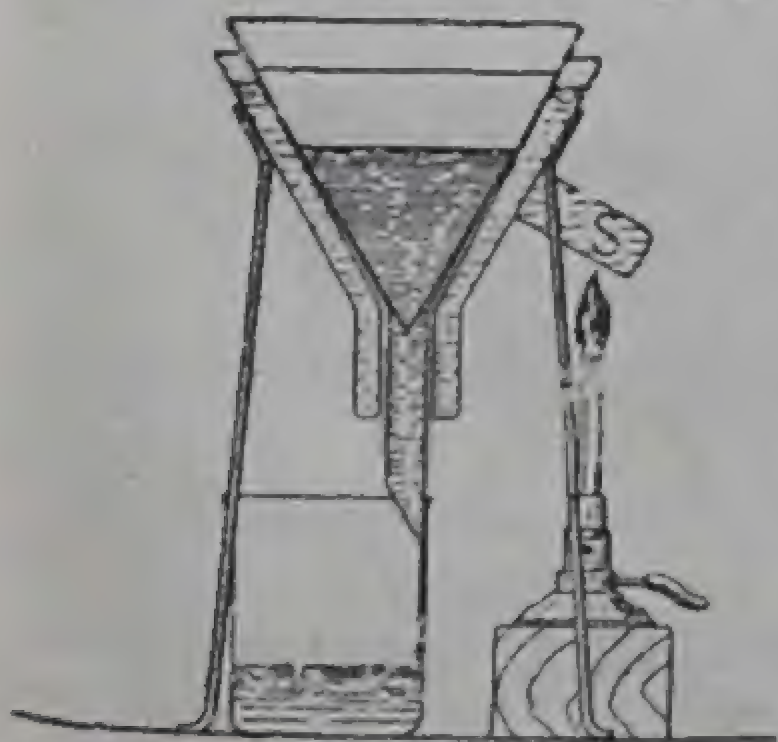


Fig. 2. Hot-water Funnel. vapour of the solvent is inflammable, the flame *must* be put out before starting the actual filtration.

(iii) *Crystallizing.* The hot filtrate is allowed to cool as slowly as possible in a beaker covered with a watch-glass, with the convex side upwards. In this manner, large, beautiful crystals are obtained. For analytical work, however, small-sized, pure crystals are required. These are readily obtained by cooling the hot solution rapidly, say, by placing the beaker in cold water. The crystals thus obtained are free from droplets of the mother liquor, which the large crystals are very liable to occlude.

In the case of certain substances, on allowing the hot solution to cool, an oily liquid may separate out instead of crystals. This indicates that the solution is too much concentrated, and the solute, therefore, begins to separate at a temperature above its melting

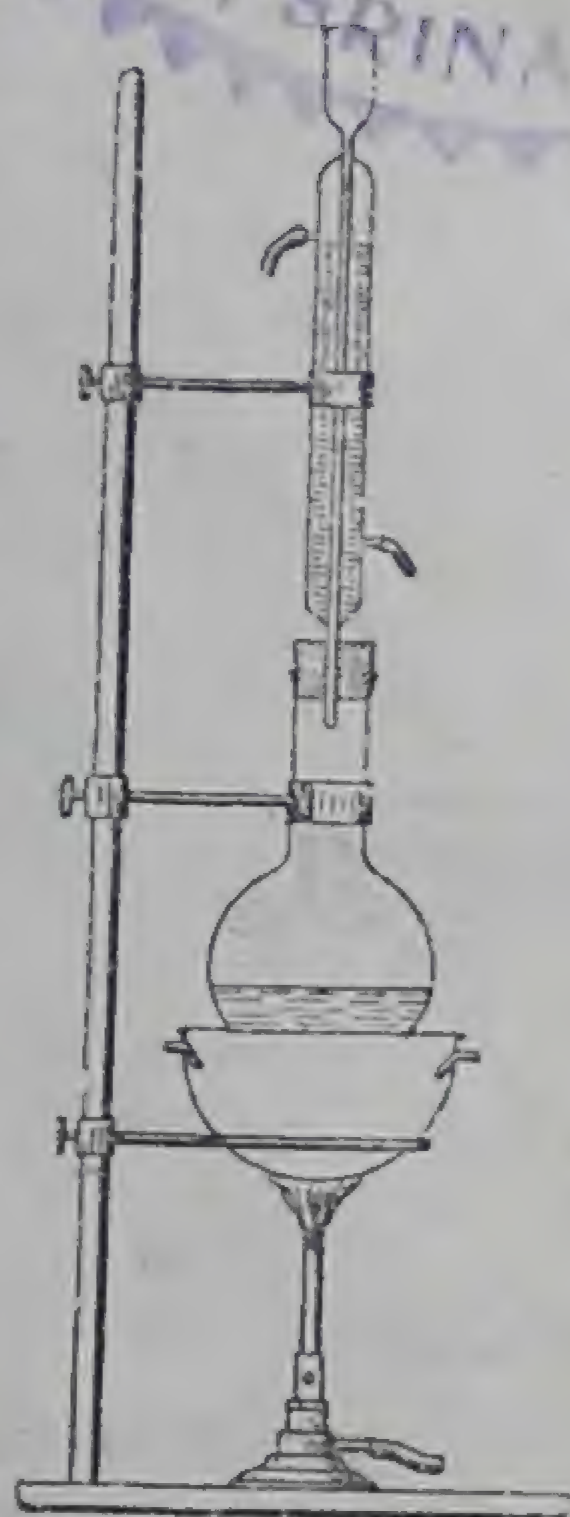


Fig. 1.

point. The defect may be remedied by adding a little more of the solvent or preparing the saturated solution below the melting-point of the solute.

(iv) *Separating Crystals from Mother Liquor.* If the crystals are large, the mother liquor can be readily poured off and the crystals washed with a little of the pure solvent. The best method, however, of separating the crystals from the mother liquor is that of filtration,

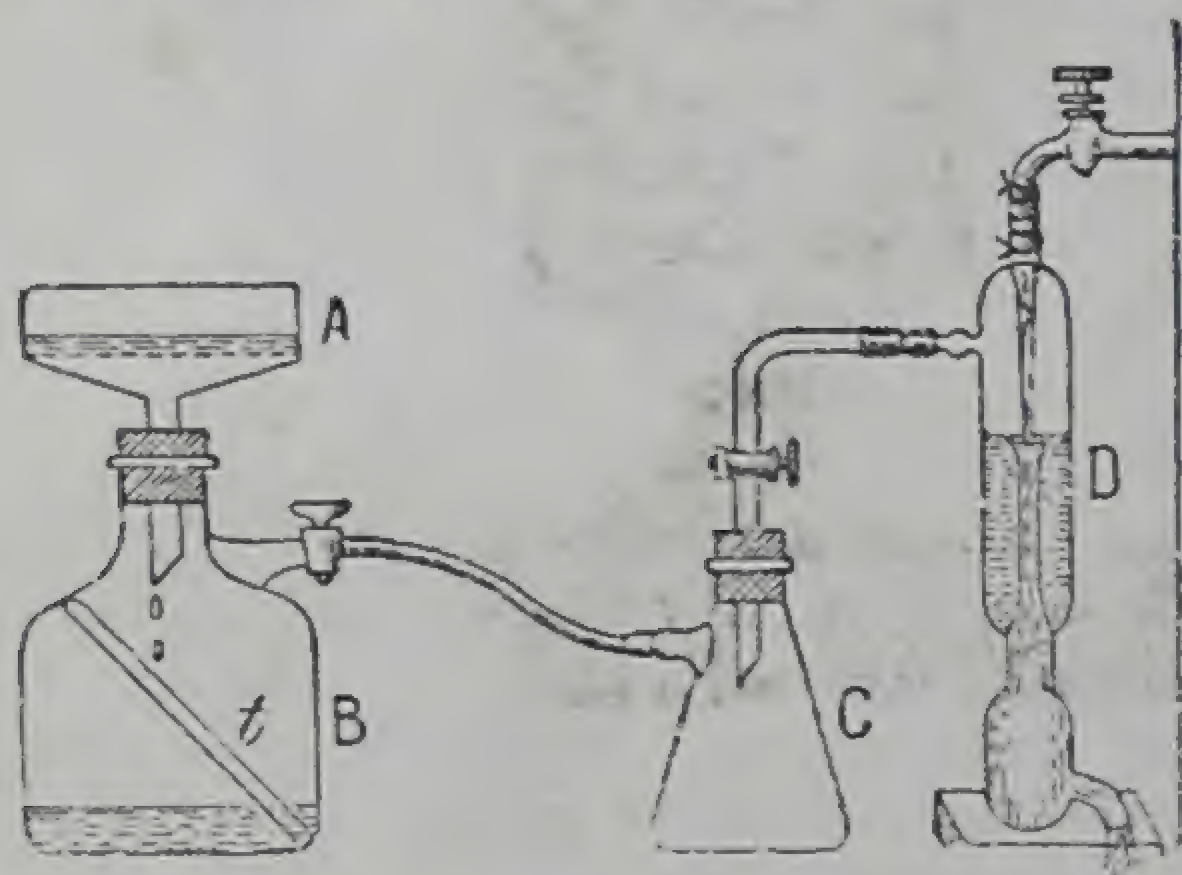


Fig. 3. Filtration under Reduced Pressure. (A) Buchner Funnel, (B) Filtering flask, (C) Trap, (D) Water Pump.

tube will be the same; but should air enter the flask, the liquid will rise into the tube, thus indicating a leakage. The trap, C, prevents the liquid left in the body of the pump, D, from being sucked into the filtering flask, B.

For handling large amounts of material in technical operations, a centrifugal machine is most frequently used.

Fig. 4 shows a centrifugal machine for drying crystals, designed by Professor Richards of Harvard University. It is specially suitable for chemical and sugar laboratories. The crystals to be dried are put into the perforated drum, D, made in this case of porcelain. The outer bucket, B, is also of porcelain and is provided with a draining nozzle, N. The drum is made to rotate at a speed of 1,000 revolutions per minute, by means of the electric motor, M. The dry crystals are left inside the drum, while the mother liquor, which previously adhered to the crystals, passes out through the perforations into the outer bucket.

Expt. 1. Dissolve an impure sample of acetanilide in hot water. Add a little animal charcoal, and filter the hot liquid, using a hot-water funnel. Allow the filtrate to cool. Acetanilide separates out in shining colourless plates. Separate the crystals, using a Buchner funnel and water pump (Fig. 3), and wash them with a little water.

using a Buchner funnel, A, and filter pump, D (Fig. 3). If the filtration be very slow, a filtering flask, B, provided with a stopcock, should be used. When the pump has been working for some time, the stopcock is closed, and the pump disconnected. A small tube, t, closed at the upper end and open at the lower, may be placed inside the filtering flask. This serves as a vacuum-gauge. So long as the vacuum is perfect inside the filtering flask, the level of the liquid inside and outside the

SOME MODIFICATIONS OF THE PROCESS OF CRYSTALLIZATION :—

(a) **Crystallization by Spontaneous Evaporation.** If the substance in hand is as soluble in the cold as in the hot solvent, it is of course not possible

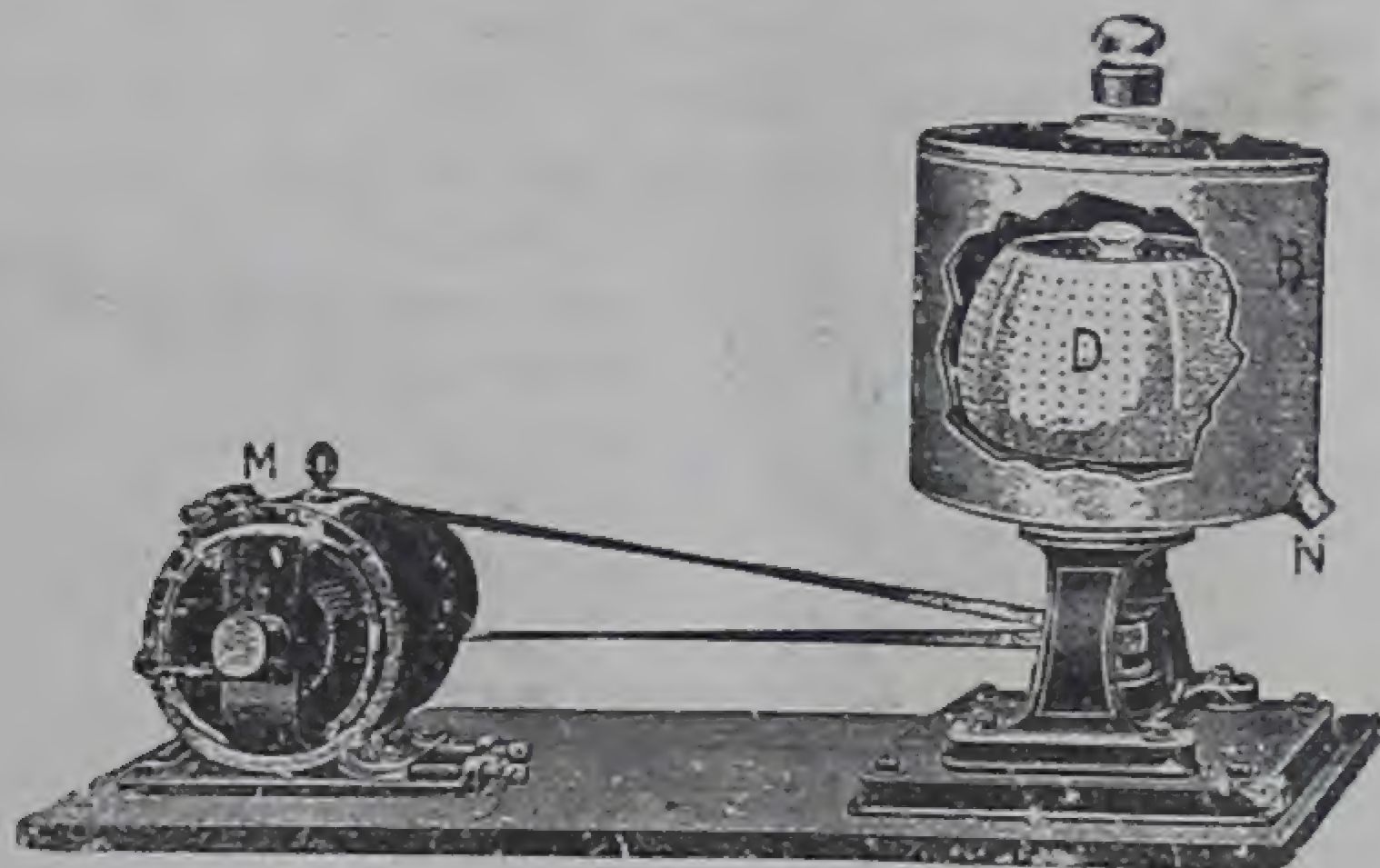


Fig. 4. Centrifugal Machine worked by Electric Motor.

to obtain crystals by allowing the hot solution to cool. In such a case the solution is allowed to evaporate spontaneously at the laboratory temperature. As the solvent gradually evaporates away, the solution becomes more and more concentrated and finally deposits crystals of the substance.

(b) **Crystallization by means of two Miscible Solvents.** If the given substance is too soluble in one solvent and insufficiently soluble in another to permit its crystallization from either of the two, it is sometimes possible to crystallize it from a mixture of both, provided they are miscible. The substance is first dissolved in the solvent in which it is readily soluble and the other solvent is then gradually added, until a slight turbidity occurs. The mixture is warmed, until it is quite clear, and then allowed to cool. Should it be necessary to crystallize by spontaneous evaporation of the solution, the solvent in which the substance is more soluble must also be the more volatile. As evaporation goes on, the solution becomes gradually richer in the second solvent and deposits crystals of the substance. Meta-dinitrobenzene is usually crystallized from a mixture of alcohol and water. It is far more soluble in alcohol than in water.

If the substance is readily soluble in water but practically insoluble in alcohol, it may be dissolved in a mixture of the two and the solution allowed to stand in a desiccator containing quicklime. The quicklime absorbs the water vapour but not the vapour of alcohol. The solution therefore gets progressively richer in alcohol and ultimately deposits crystals of the substance.

The following pairs of solvents are frequently employed for crystallization in the manner described :—

- (i) Alcohol and water,
- (ii) Benzene and petroleum ether,
- (iii) Chloroform and petroleum ether,
- (iv) Alcohol and ether.

(2) **Fractional Crystallization.** The method of simple crystallization is only suitable for the purification of a single substance, contaminated with *small* quantities of impurities. When it is desired to separate two (or more) substances, both of which are soluble in the solvent used, the method of *fractional crystallization* must be employed. Three different cases arise:—

(i) *The substances differ considerably in their solubilities.* In such a case it is usually easy to find a solvent which will dissolve a large portion of the more readily soluble constituent and but a little of the less soluble. If we treat the mixture with a suitable quantity of the solvent, we will get a solution that contains practically the whole of the readily soluble constituent, *A*, with but a little of the difficultly soluble constituent, *B*. The solution is filtered from the residual solid. Thus we are able to resolve the mixture into two fractions: (i) the solution, and (ii) the residue.

The solution is now evaporated to a certain point; *B* crystallizes out, unaccompanied by any of the *A*. The crystals of *B* are filtered out, and the solution is allowed to evaporate in order to get crystals of *A*.

The crystals of *B* and the residue from the first operation are dissolved in a fresh quantity of the solvent. On evaporating, *B* will crystallize out practically free from *A*.

On repeating the crystallization of the two fractions a second time, we get a practically complete separation of *A* and *B*.

(ii) *The substances possess nearly equal solubilities, but the proportion of the one is considerably greater than that of the other.* The separation of such a mixture is also comparatively easy. On cooling the hot solution of the two substances in a suitable solvent, the constituent present in larger quantity crystallizes out first. After standing for some time, the solution may deposit crystals of the second substance. In such a case the crystallization must be carefully watched, and as soon as crystals differing from those that separated out first make their appearance, the solution, even though still warm, is immediately filtered with suction.

(ii) *The substances possess nearly equal solubilities and are present in nearly equal proportions.* In such a case the crystals of the two compounds appear side by side, and must be separated mechanically. For instance, if one of the substances separates in big crystals and the other in small ones, separation can be readily effected by sifting through a suitable sieve. Sometimes, difference in specific gravity of the two kinds of crystals is utilized for their separation. A rotatory motion is imparted to the mother liquor by rapidly stirring with a

glass rod. The lighter crystals thereby rise to the top of the liquid, while the heavier ones collect at the bottom of the vessel. The mother liquor with the lighter crystals floating in it is rapidly poured off. As a last resource, the two compounds may be separated by picking out the individual crystals by hand.

(3) **Sublimation.** Certain substances are converted by heat into vapours, which, when condensed on a cold surface, do not pass into the liquid state, but deposit directly in the form of crystals. The process is known as sublimation. Some of the substances which can be readily purified by this process are:

Naphthalene,

Camphor,

Anthracene,

Benzoic Acid.

A simple method of sublimation consists in placing the substance to be sublimed on a watch-glass heated very slowly on a sand-bath with a free flame. The watch-glass is covered with an inverted funnel, somewhat smaller than itself (Fig. 5). Over the edge of the funnel is stretched a perforated filter paper. This prevents the small, light crystals of the substance from falling back on to the watch-glass. The upper surface of the funnel may be kept cool by covering it with several layers of wet filter paper.



Fig. 5. A simple apparatus for sublimation.

A very efficient apparatus for sublimation is that designed by Bruhl (Fig. 6). This consists of a hollow, metallic vessel provided with inlet and outlet tubes for circulating water, and having in the middle an opening of the shape of an inverted truncated cone. The substance to be sublimed is placed in a crucible supported in the opening as shown in the figure, and the whole is covered with a glass dish. The substance sublimes in part on the inside of the glass dish, but more abundantly on the upper, cold surface of the metallic vessel.

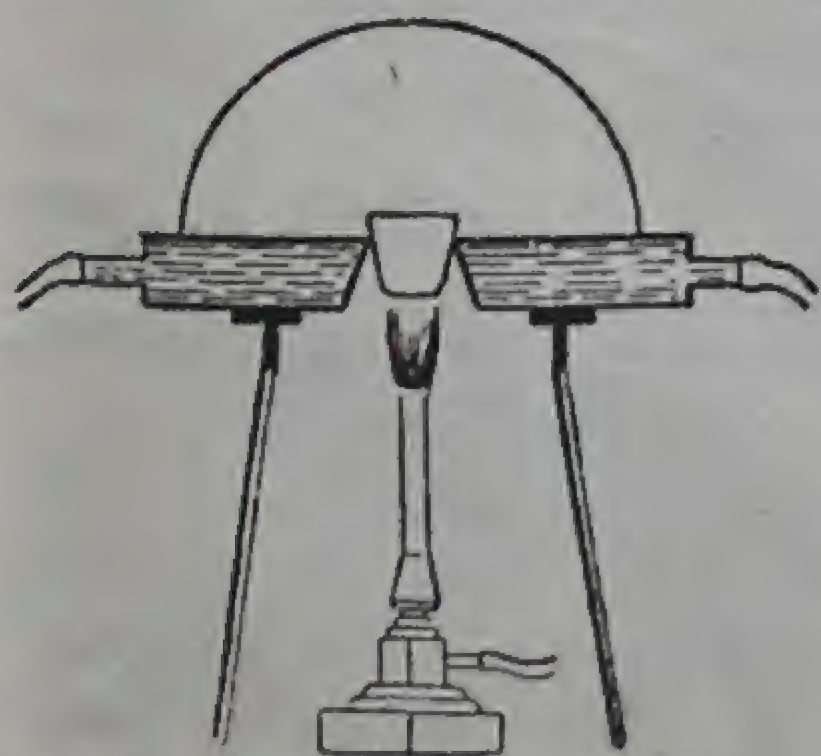


Fig. 6. Bruhl's Sublimation Apparatus.

Expt. 2. Using the apparatus sketched in Fig. 5, or Fig. 6, prepare a sample of pure benzoic acid or anthracene.

(4) **Distillation.** Distillation is the process of converting a liquid or solid into a vapour, which is then condensed. When a solid is distilled, we do not get the crystals directly, as is the case in sublimation. The distillate is a liquid which may subsequently solidify into a crystalline mass. The process of distilla-

tion is used for freeing a volatile substance from non-volatile impurities, or from substances which are far more or far less readily volatile than the substance to be purified.

The usual form of apparatus employed in distillation is shown in Fig. 7. It consists of:—

- (i) a distillation flask, *F*, provided with a side-tube,
- (ii) a Liebig condenser, *C*, and
- (iii) a receiver, *R*.

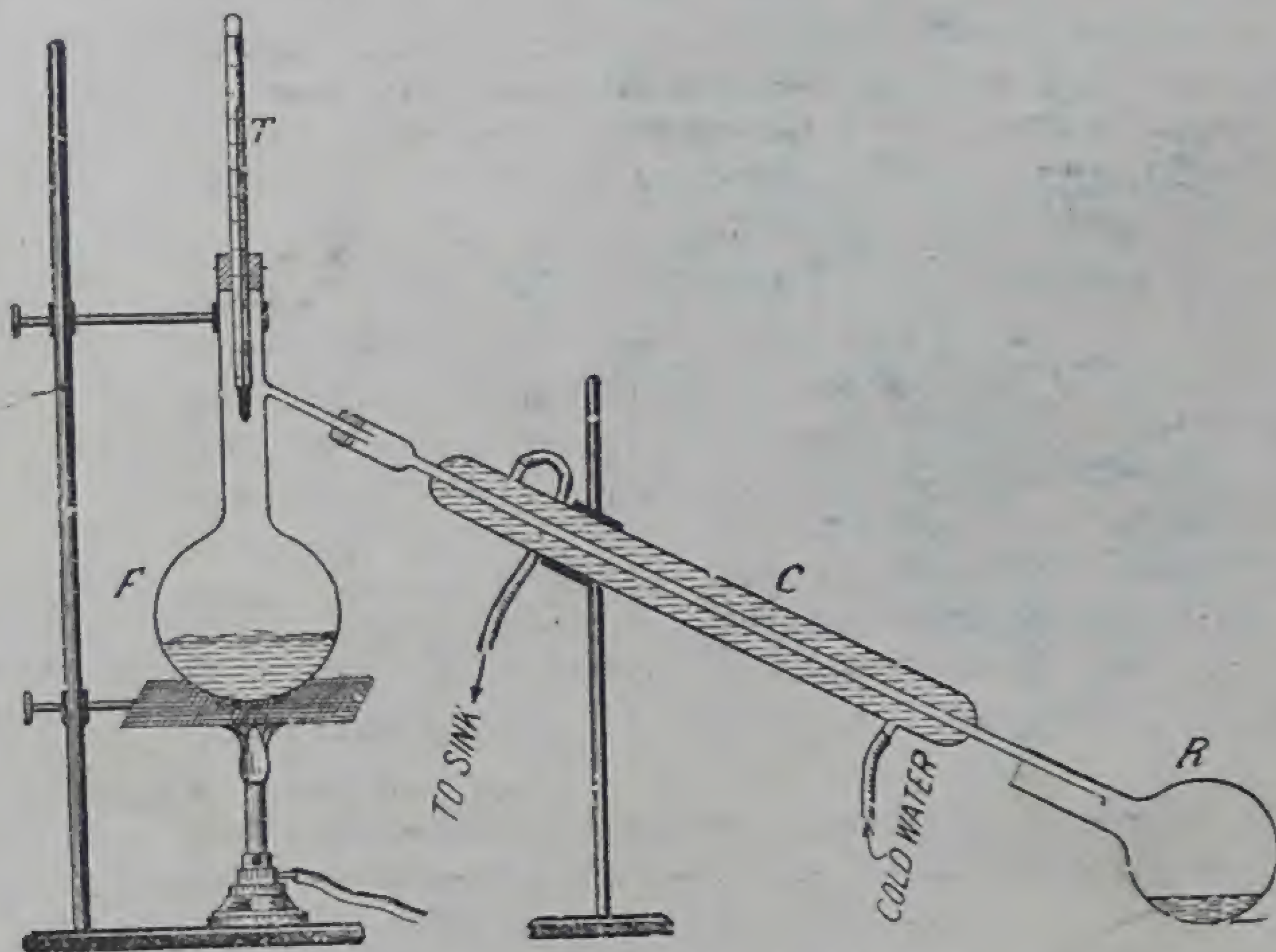


Fig. 7. Distillation Apparatus.

A thermometer, *T* is usually fitted into the neck of the flask in order to note the boiling-point of the liquid. The bulb of the thermometer must be just below the position where the side-tube is fused into the neck of the flask. The end of the side-tube of the distillation flask must pass right through the cork, so that the distillate, as it falls into the condenser tube, does not come into contact with the cork. To prevent the liquid from “bumping” (sudden, violent ebullition), a few pieces of broken porous tile (or some glass beads) are added to it before starting the distillation.

In case the object is not to determine the boiling point, but to distil a fairly large quantity of the liquid, the thermometer may be replaced by a dropping funnel. From this the liquid to be distilled is made to drop continuously at the same rate as that at which the distillate passes.

When the boiling-point of the liquid lies about 170°C , there is great danger of the condenser tube getting cracked. In such a case, therefore, a straight glass-tube, called an *air-condenser* (Fig. 8) is used instead of the water-cooled condenser.

Expt. 3. Using the apparatus given in Fig. 7 distil some pure benzene. Add a few pieces of porous tile to prevent bumping. Notice that practically the *whole* of benzene passes over at a constant temperature (*i.e.*, 80 to 80.5° , depending upon the atmospheric pressure).

Expt. 4. Using an air-condenser, distil some aniline, which has turned dark in colour. Notice that the first few drops are turbid because of the presence of moisture. As soon as the distillate passes clear, receive the aniline (b. p. 183°) into a clean dry flask.

(5) **Fractional Distillation.** This process is employed for separating a mixture of two or more miscible liquids, the boiling points of which are sufficiently removed from one another. The method is similar to ordinary distillation, except that portions of the distillate passing at different temperatures are collected separately. The boiling must be made to proceed slowly and evenly, so that it may be possible to count the individual drops as they fall into the receiver.

On distilling a mixture of two liquids, say, benzene (b.p. 80°) and toluene (b.p. 111°), more of the lower boiling liquid passes over at the beginning and more of the higher boiling one at the end, of the operation, the composition of the distillate changing continuously. In order to effect a separation of benzene-toluene mixture, the distillate may be best collected in 5 fractions: *A* from 80° to 85° ; *B*, from 85° to 91° ; *C*, from 91° to 98° ; *D*, from 98° to 105° ; *E*, from 105° to 111° . The different fractions are collected in labelled flasks, and their respective volumes noted. The portion of the liquid which does not distil up to 111° is rejected.

The process of distillation is now repeated as follows: The contents of flask *A* are transferred to the distillation flask and redistilled, the distillate passing at 80° to 85° being collected in the same flask, *A*. When the temperature reaches 85° , the distillation is stopped and the contents of flask *B* added to the distillation flask. The distillation is continued once again, and the fraction passing at 80° to 85° is collected in flask *A* and from 85° to 91° in the flask *B*. As soon as the temperature reaches 91° , the distillation is again stopped and the contents of flask *C*, added. The distillation is once more continued and the fraction passing at 80° to 85° , 85° to 91° and 91° to 98° are



Fig. 8. Air Condenser.

collected in flasks *A*, *B* and *C* respectively. The process is carried on in the above manner, until all the fractions have been added.

The five fractions collected during the second distillation are submitted to the same process as before and the operation repeated a number of times. Each time the fractionation is repeated, the volumes of the fractions *A* and *E* increase, while those of fractions *B*, *C* and *D* continuously decrease. When the total amount of the liquid in flasks *B*, *C* and *D* becomes very small (say less than one-tenth of the total amount of the liquid) the refractionation may be stopped.

The process of fractional distillation may be carried out in a fractionating flask, *i.e.*, a distillation flask with a sufficiently long neck. If large quantities of a mixture are to be handled, an ordinary round-bottomed flask of a suitable capacity can be converted into a fractionating flask by using a fractional-distillation tube, as shown in Fig. 9. The process of fractionation, however, is rendered more efficient and rapid by using a fractionating column (Fig. 10), connected to the neck of the boiling flask. The fractionating column aids the separation by working in the opposite way to the boiling process. As the vapour passes upwards through the column, it gets partially condensed by the cooling action of the air. The condensate flows down the column, and forms a layer around each disc, glass-bead, or ring contained in the column. In this manner the up-going vapour is brought into a continuous contact with the down-flowing liquid, whereby the vapour is thoroughly scrubbed. The scrubbing aids the separation both by partial evaporation of the liquid and by partial condensation of the vapour; there occurs a continuous exchange of constituents between the vapour and the liquid. Thus, by the time the vapour reaches the top of the column, most of the less volatile constituent

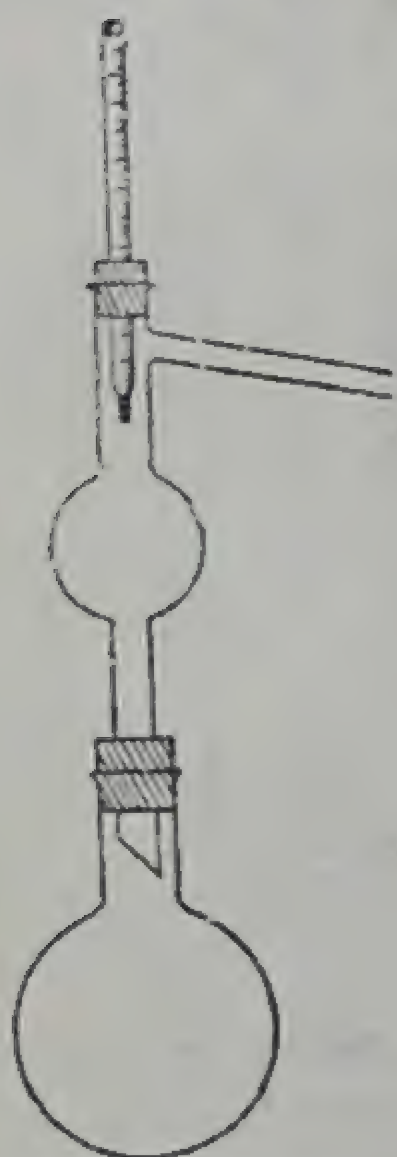


Fig. 9. Round-bottom flask fitted with Fractional-Distillation Tube and Thermometer.

has been condensed. Similarly, the more volatile constituent contained in the down-flowing liquid will be completely removed by the time the latter flows down into the distillation flask. In this manner a far more thorough separation of the constituents is effected than is possible with an ordinary long-necked distillation flask. The use of a fractionating column renders the number of distillations much smaller, though, as a rule, it cannot entirely do away with the necessity of redistilling.

The various types of fractionating columns used in the laboratory are shown in Fig. 10; of these, the most efficient is the one packed with Lessing's contact rings.

Expt. 5. Using a long fractionating column packed with Lessing's contact rings made of aluminium, or with small pieces of glass tubing, distil a 1 : 1 mixture of benzene and toluene. Collect 5 fractions and measure their respective volumes. Repeat the fractionation a second time.

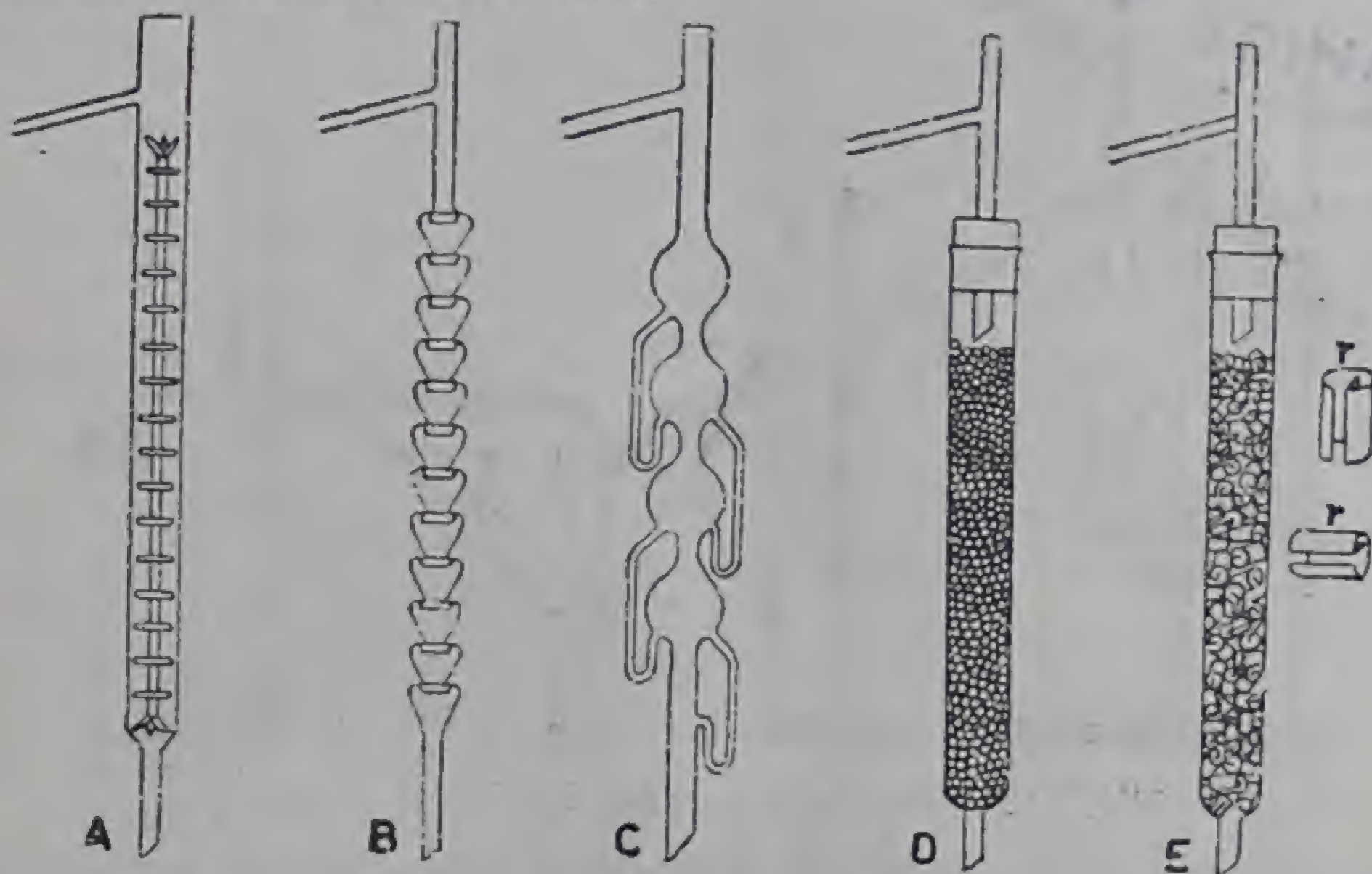


Fig. 10. Different types of Fractionating Columns.

(A) Young's rod-and-disc type ; (B) Young's pear-shaped type ; (C) Le Bel-Henninger column ; (D) Hempel's column filled with glass beads ; (E) Still head filled with Lessing's contact rings *r*, *r* (shown on a large scale on the right of E).

For the separation of mixtures of volatile liquids on a commercial scale very carefully designed fractionating columns are used, which may attain a height of 30 feet or more. The Coffee still used for rectifying aqueous alcohol, the long air-cooled vertical columns employed for the separation of crude petroleum into various fractions, and the plant employed for the fractionation of 90 per cent and 50 per cent benzol, to obtain pure benzene, toluene and xylene, are important examples of the use of fractionating columns in chemical industries.

(6) **Distillation under Reduced Pressure.** Some organic liquids which decompose at their boiling points under atmospheric pressure may be distilled without decomposition under low pressure. Thus glycerine boils with partial decomposition at 290° under 760 mm. pressure. It may be distilled without decomposition at 180° under a pressure of 12 mm.

The usual form of apparatus used in vacuum distillation is shown in Fig. 11. The liquid distilled is placed in a Claisen's distillation flask, *F*. Through one of the necks of the flask passes a thermometer, *T*, and through the other a glass tube, *C*, which is drawn out at its

lower end to a capillary dipping into the liquid, and is closed at its upper end by means of a piece of rubber tubing and a screw clamp.

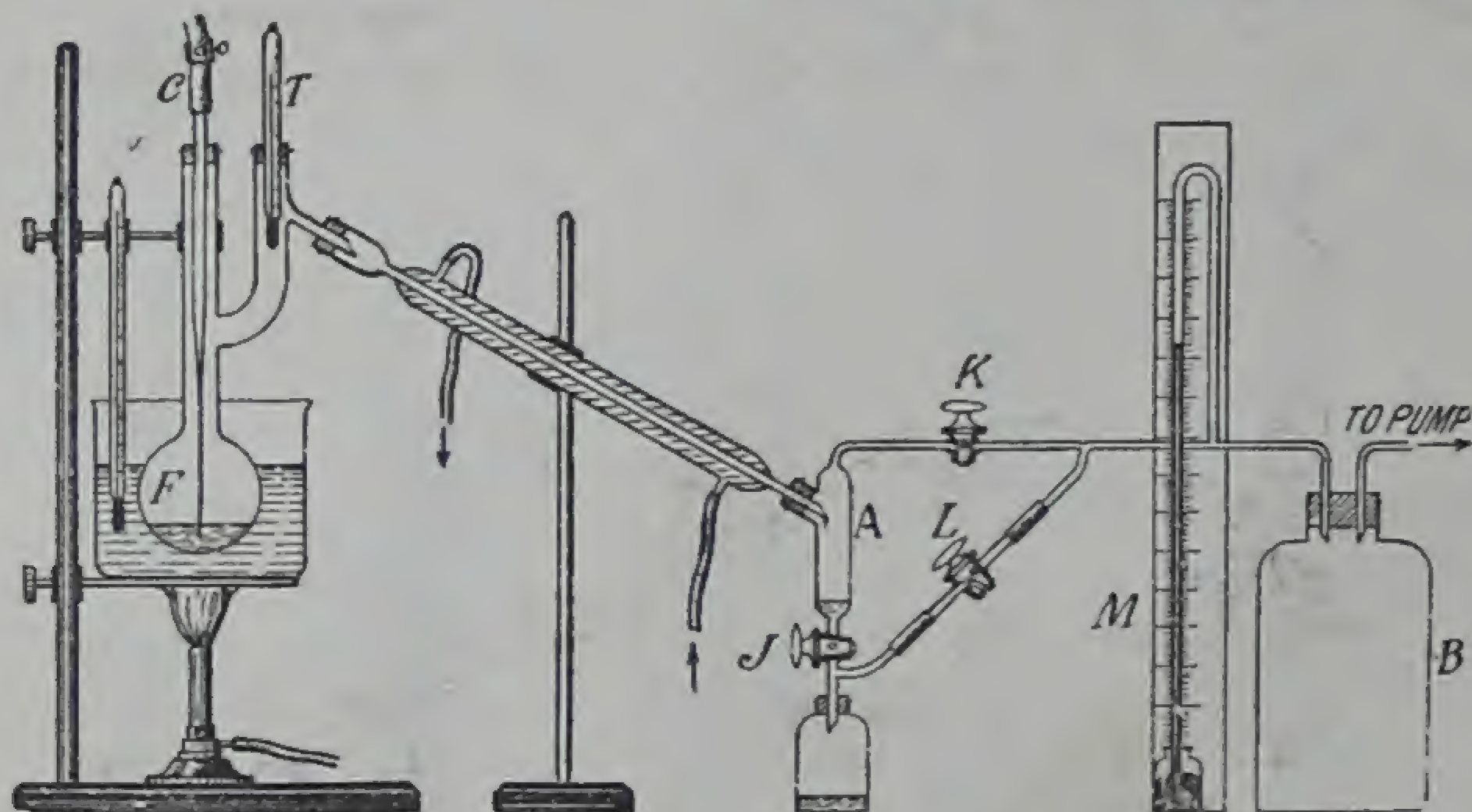


Fig. 11. Distillation under Reduced Pressure.

This arrangement prevents bumping, which is more pronounced during vacuum distillation than during distillation under ordinary pressure. The evacuation of the apparatus is effected by means of a water or mercury pump. In the former case, the lowest pressure obtainable is that of aqueous vapour at the room temperature (*i.e.*, usually 10 to 25 mm.). With a mercury pump, pressures lower than 1 mm. can be readily obtained. A manometer, *M*, is introduced between the receiver and the pump to ascertain the pressure under which the distillation takes place. All corks must be made perfectly air-tight by coating them with collodion after the apparatus has been fitted up.

In most of the distillations under reduced pressure it is necessary to collect the distillate in fractions. Many ingenious forms of receiver have been devised, so as to allow the collection of various fractions without breaking the vacuum. The best known of these arrangements is the triangle apparatus shown in Fig. 11. When it is desired to change the receiver, the cock, *J*, is turned off, *K* is turned on, while the three-way cock, *L*, is turned so that the receiver is put in communication with the outside air and not with the pump, meanwhile the distillate goes on collecting in *A*. The receiver is now changed, the cock *L* is turned, so that the receiver is once again put into communication with the pump. After a short time, the cock *K* is closed and *J*, opened, so that the distillate in *A* flows down into the new receiver.

(7) Steam Distillation. The process of steam distillation is employed for separating those substances which are appreciably

volatile at 100° from non-volatile components of a mixture. The apparatus employed is shown in Fig. 12. The mixture to be treated is placed, along with some water, in a large-size round-bottom flask, *F*, heated on a sand-bath and connected to a condenser, *C*.

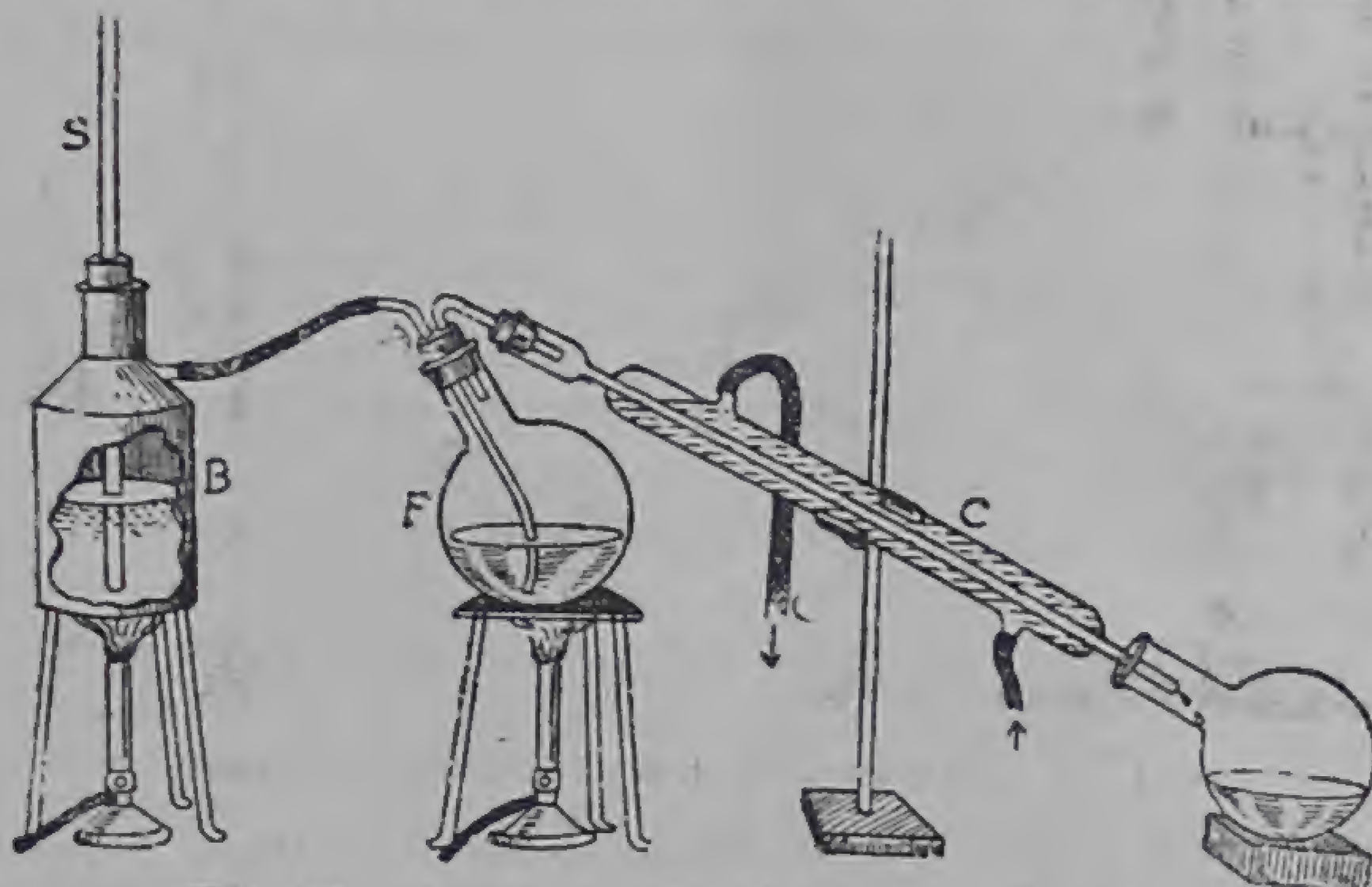


Fig. 12. Apparatus for Steam Distillation.

The flask is held in a sloping position, so that during the vigorous ebullition, which occurs, none of the mixture may be thrown up into the tube leading to the condenser. Steam from the boiler *B* (which generally consists of a tin can provided with a safety tube, *S*), is rapidly passed through the liquid in the flask *F*. The heating of *B* and *F* are controlled, so as to keep the quantity of the liquid in *F* constant. In the case of an oily liquid, or a solid substance, the distillation should be continued for about 15 minutes after drops of oil or particles of solid have ceased to appear in the condenser. In the case of a soluble acid, the distillation should be stopped when the distillate no longer gives an acid reaction with litmus.

The distillate in the receiver consists of water and the substance whose separation is desired. In case the substance is an oily liquid, it is separated from the water by means of a separating funnel (Fig. 13); if it is an insoluble solid, it is separated by filtration. If the substance is a soluble acid, the liquid is

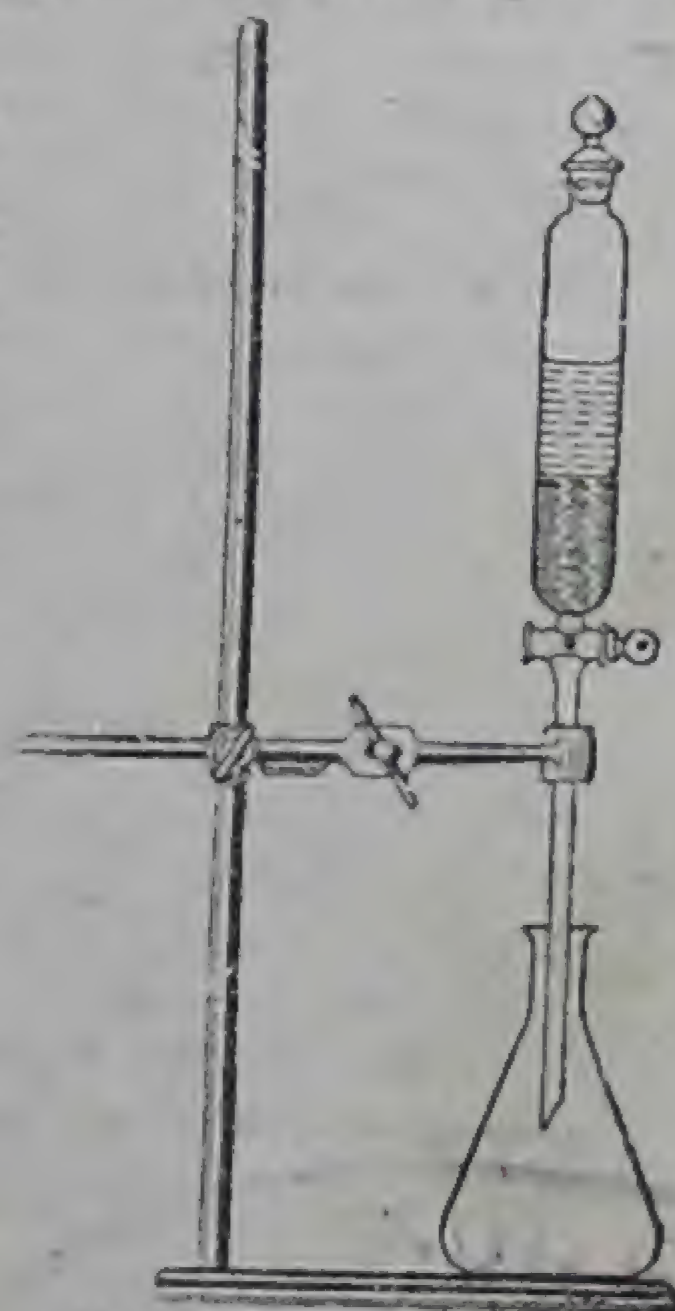


Fig. 13. Separating Funnel.

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exactly neutralized with sodium carbonate, and the solution evaporated to dryness. From the pure sodium salt, thus obtained, the acid may be recovered by distilling with sulphuric acid. The substances usually purified and separated by the process of steam distillation are aniline, bromobenzene, *p*-dibromobenzene, essential oils, petroleum, turpentine oil, etc.

Expt. 6. (a) Fit up the apparatus shown in Fig. 12. Place some well-powdered *ajwain*, made into a thin paste with water, into the flask *F*. Carry on the steam-distillation of the substance, until no more oily drops of *ajwain* oil pass over. Separate the oil by means of a separating funnel (Fig. 13).

(b) Carry out the steam distillation of the oleo-resin of turpentine (*ganda baroza*). The distillate consists of *turpentine oil* and water; the residue consists of *rosin*.

The *ajwain* oil, on fractional distillation, gives *thymol*, a colourless crystalline substance, used as a mild antiseptic, and certain hydrocarbons, called *thymenes*, which are used as a soap perfume.

PRINCIPLE OF STEAM DISTILLATION. In the process of steam-distillation two volatile substances take part: (i) water, and (ii) the substance whose separation is desired. In case the two substances are mutually immiscible, the vapour pressure of each is unaffected by the presence of the other. When the mixture is boiling, the sum of the vapour pressures p_1 and p_2 of the constituents must equal the atmospheric pressure, P . That is,

$$P = p_1 + p_2.$$

The boiling point of the mixture must, therefore, be even lower than that of the lower boiling constituents at the atmospheric pressure. Hence, in steam-distillation the same object is achieved as in distillation under reduced pressure, *i.e.*, the boiling of a substance is effected at a temperature lower than its actual boiling point at the atmospheric pressure.

The relative quantities of water and the liquid that is steam-distilled, w_1 and w_2 , which pass over, are proportional to (i) their relative-partial pressures p_1 and p_2 , at the temperature of distillation, and (ii) their relative vapour densities or molecular weights. Now, the molecular weight of water is 18. If M is the molecular weight of the substance that is being steam-distilled, we have:

$$\frac{w_1}{w_2} = \frac{p_1 \times 18}{p_2 \times M}.$$

Example. What weight of aniline, $C_6H_5NH_2$, will be carried over by 100 gm. of steam at $99.4^\circ C$, the atmospheric pressure being 760 mm. The aqueous tension at $99.4^\circ C$ is 747 mm.

Molecular weight, M , of aniline, $C_6H_5NH_2 = 72 + 5 + 14 + 2 = 93$.

Partial pressure, p_1 , of steam = 747 mm.

Partial pressure p_2 , of aniline = $760 - 747$ mm. = 13 mm.

Weight of aniline, w_2 , carried over by 100 gm. of steam at $99.4^\circ C$

$$= 100 \times \frac{p_2 \times M}{p_1 \times 18}$$

$$= 100 \times \frac{13 \times 93}{747 \times 18} = 8.99 \text{ gm.}$$

(8) **Dialysis.** This process is employed for the separation of crystalloids from colloids. The mixture is placed in a *dialyser*, an apparatus consisting of a shallow glass cylinder over the lower end of which is stretched a parchment paper or a piece of muslin impregnated with collodion (Fig. 14). The dialyser is made to float in a trough of pure water, which is changed from time to time. The crystalloid molecules diffuse out through the parchment paper, while the colloid remains behind in the dialyser.

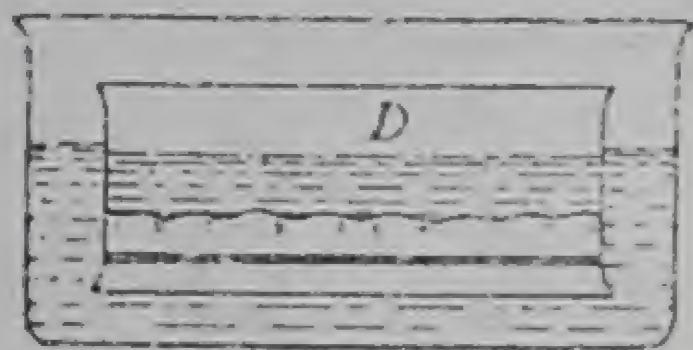


Fig. 14. Dialysis.

The “diffusion process” for the manufacture of cane-sugar from beets and the recovery of cane-sugar from molasses are examples of the application of dialysis in technical organic chemistry.

(9) **Extraction with Solvents.** The process of extraction with solvents is employed in the following three cases :—

(i) *Isolation of a Substance Dissolved or Suspended in a Liquid* (usually Water). The separation of the substance is effected by agitating the liquid with a solvent in which the substance is more readily soluble but which is not miscible with the first liquid, drawing off the solution of the substance in the new solvent, and distilling off the latter. The most commonly used solvent for this purpose is ether, though, in certain cases, carbon disulphide, petroleum ether, chloroform and benzene, are also used.

A familiar example of ether extraction is that of aniline. This substance is prepared by the reduction of nitrobenzene, and is separated from the reaction mixture by steam-distillation. The distillate separates into two layers : a lower layer of aniline, and an upper layer consisting of an aqueous solution of aniline, which also contains a quantity of aniline in the form of minute droplets that do not settle quickly (*i.e.*, an emulsion). The lower layer can be separated by means of a separating funnel, and presents no difficulty. To recover aniline from the aqueous layer, it is shaken up with ether, in which aniline is much more soluble than in water, and the upper ethereal solution of aniline is separated from the lower aqueous layer by means of a separating funnel. The lower aqueous layer is once again shaken up with a little more of ether, and the ethereal layer again separated. Finally, aniline is recovered by boiling off the ether.

(ii) *Isolation of a Substance from a Solid Material.* The more important examples of extraction of this type are : the extraction of alkaloids from leaves and bark of plants, of flavouring extracts from seeds and of oils from crushed seeds and oil cake.

The Soxhlet Extractor (Fig. 15), which is frequently used in chemical laboratories for the extraction and estimation of fat or oil

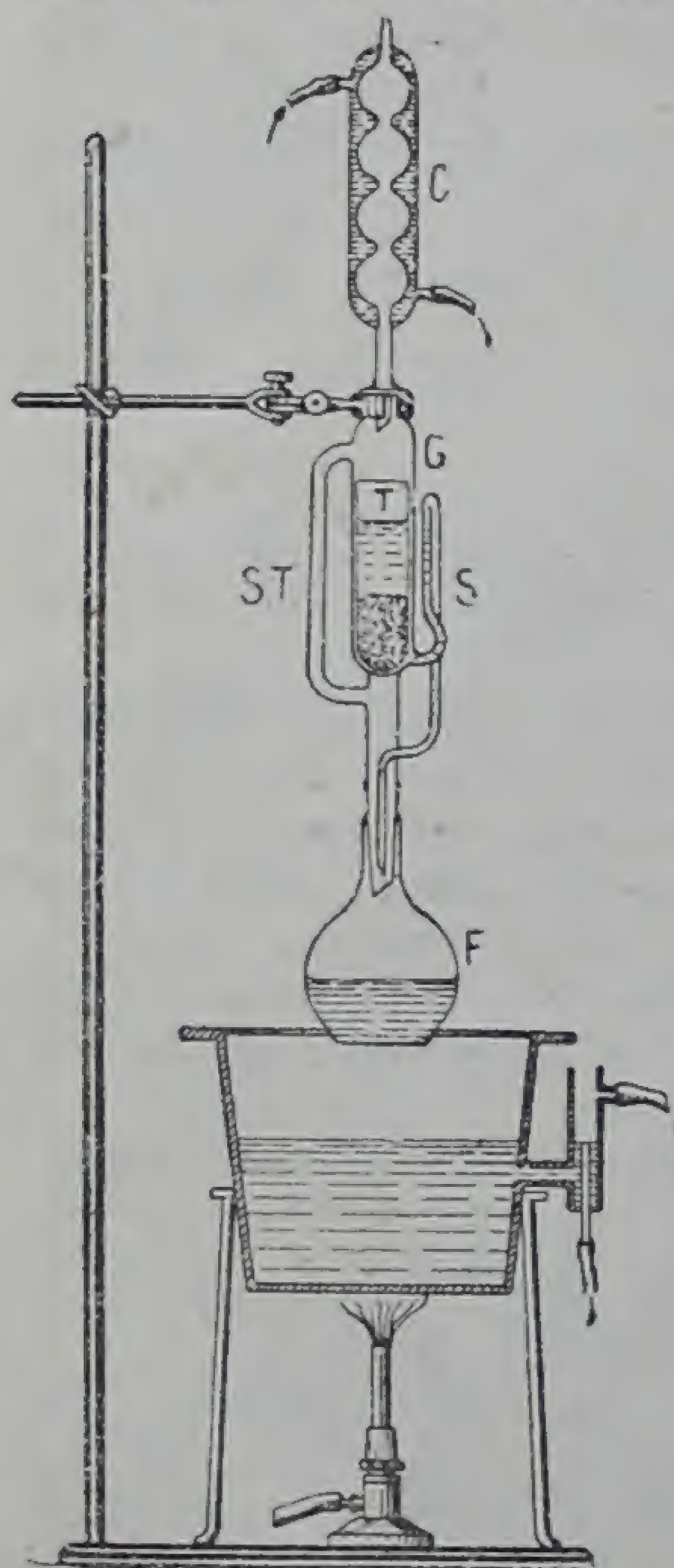


Fig. 15. Soxhlet Extractor.

Expt. 7. Arrange the Soxhlet extractor on a water-bath. Introduce a weighed quantity of crushed cocoanut into a thimble or a filter paper cylinder. Use petrol as the extracting solvent. The upper end of the condenser should preferably be provided with a long piece of rubber tubing to carry off the uncondensed inflammable vapour of petrol to a hood or waste-sink. At the end of the operation evaporate off the petrol, and weigh the residual cocoanut oil.

(iii) *Removal of Soluble Impurities from Mixtures.* This is of great importance in the purification of organic substances. The principle involved is similar to (ii), except that the solvent extracts the impurities, leaving behind the desired substance in a more or less pure condition. Here, as in (ii), several extractions with small portions are more effective than a single extraction with the whole of the given quantity of the solvent.

in a material, *e.g.*, oil seeds and oil cake, is a very convenient apparatus for this purpose. The powdered material is put into a *thimble*, *T*, made of stout filter paper and placed inside the glass tube, *G*. The latter is provided with a syphon, *S*, and a side-tube, *S. T.* The length of the thimble should be such that it extends about 1 cm. above the highest point of the syphon tube. The amount of solvent taken in the boiling flask *F*, should be $1\frac{1}{2}$ to 2 times the volume of *G* up of the highest point of the syphon. The flask *F* is heated on a water-bath or sand-bath according to the nature of the solvent. The vapour of the solvent rises through the side-tube up into the water-cooled condenser, *C*. The condensate drops into the thimble, dissolves the substance, and filters out into the space between the thimble and the glass tube. As soon as the liquid level in *G* reaches the highest point of the syphon, the solution automatically flows back into the boiling flask. The process may be continued for as long a time as necessary. At the end of the operation, the solvent is boiled off, and the isolated substance weighed, if necessary.

Distribution Law. The process of extraction with solvents is based on the distribution law or *partition law*. If we shake up a substance with two immiscible solvents, say succinic acid with ether and water, it will distribute itself between the two solvents in such a manner that a definite ratio is maintained between the two concentrations, *i.e.*,

$$\frac{\text{Concentration of solute in ether}}{\text{Concentration of solute in water}} = K$$

This ratio is called the *partition coefficient* of the substance for the two solvents. Its value for the distribution of succinic acid between water and ether at 15°C is 5.4. It can be readily shown that a given amount of a solvent will effect a more complete extraction when used in several small portions than when used in one lot.¹

Expt. 8. Dissolve some iodine in a dilute solution of potassium iodide. Shake the solution in a test-tube with a few drops of carbon disulphide. Notice that the latter solvent takes up most of the iodine, and forms a violet coloured layer at the bottom. The partition coefficient of iodine for carbon disulphide and water is over 400.

(10) **Salting Out.** Many organic substances which are soluble in pure water are insoluble or sparingly soluble in aqueous solutions of certain salts, notably sodium chloride, potassium carbonate, calcium chloride, and Glauber's salt. Hence, when a solid salt is added to an aqueous solution of an organic substance, *e.g.*, ethyl alcohol, acetone, aniline, pyridine, etc., the substance is thrown out of solution and may be separated by means of a tap funnel, or preferably, by extraction with ether.

A combination of salting-out and ether-extraction has many advantages. The addition of the salt to the aqueous solution before extraction with ether helps the extraction (i) by partially throwing the dissolved substance out of solution, (ii) by exchanging water with a new solvent, *viz.*, the salt solution, in which the substance is much less soluble than in pure water, the partition coefficient, WATER/ETHER, being thereby greatly reduced, and (iii) by lowering the solubility of ether in water, and thus making a larger proportion of ether available for extraction.

Salting out of ionized organic substances, *e.g.*, soap and sodium benzene-sulphonate, by common salt is due not only to the change of the solvent, but to the *common-ion effect*. The addition of the salt greatly increases the concentration of the sodium ion, whereby the solubility product of sodium benzene-sulphonate, etc., is exceeded, and the substance is, therefore, thrown out of solution.

(11) **Treatment With Animal Charcoal.** Animal charcoal finds considerable application in organic chemistry to free a colourless substance from coloured impurities, and also impurities of a tarry

¹ See "*Advanced Course of Chemical Calculations*", by Niranjana Singh and Jagindar Singh, page 108, Example 2.

character. The substance in the liquid state, or in solution with a suitable solvent, is boiled with the requisite quantity of animal charcoal and filtered. If the solvent used (or the substance itself, if liquid) be immiscible with water, the animal charcoal, which is generally moist, is dried on a water-bath before use.

In some petroleum refineries a specially prepared paddy-husk charcoal is used for decolorizing lubricating oils and melted paraffin wax. Another very efficient substitute for animal charcoal, which is much used for refining sugar in Germany, is a mixture of fine wood-meal and floated infusorial earth (*kieselguhr*). Its decolorizing power is said to be far greater than that of animal charcoal.

Expt. 9. Boil a solution of brown sugar in water (or a weak solution of magenta) with animal charcoal in a dish, and filter. Notice that the filtrate is colourless.

(12) **Drying of Organic Substances.** No organic substance can be regarded as pure, if it contains even traces of moisture. The drying of starting materials and of finished preparations is, therefore, an important feature of organic practical work.



Fig. 16. Vacuum Desiccator.

Solid substances are dried in a number of ways. If sufficiently stable, they may be dried in a steam-or air-oven or by heating on a free flame. If unstable on heating, the substance is allowed to stand in the air, or, better still, in a vacuum desiccator (Fig. 16) containing a suitable drying agent.

Before a solid substance is finally dried as given above, the adhering moisture must be removed (i) by pressing it between folds of filter paper, (ii) by pressing it on an unglazed porcelain plate, or (iii) by means of a centrifuge (Fig. 4).

Organic liquids, or solutions of organic solids and liquids in suitable solvents, are dried by letting the liquid stand in contact with a suitable drying agent. The drying agent employed in a particular case must satisfy the following conditions:—

(i) It must be practically insoluble in and chemically indifferent towards the liquid to be dried;

(ii) It must remove water efficiently:

A list of suitable desiccating agents for different classes of organic substances is given below:

Substances	Desiccating Agents
1. Hydrocarbons and Ether.	Anhydrous calcium chloride, metallic sodium, phosphorus pentoxide.
2. Alcohols.	Quicklime, anhydrous potassium carbonate, anhydrous magnesium sulphate or sodium sulphate.
3. Haloid Derivatives.	Anhydrous calcium chloride, anhydrous magnesium sulphate or sodium sulphate.
4. Aldehydes and Ketones.	Anhydrous magnesium sulphate or sodium sulphate, anhydrous calcium chloride.
5. Organic Acids.	Anhydrous magnesium sulphate or sodium sulphate, phosphorus pentoxide.
6. Organic Bases.	Solid potassium hydroxide, quick-lime or soda-lime.

As a rule, *the spent drying agent is separated before distilling off the dried liquid.* If this point is not attended to, the hydrate of the salt produced during desiccation may be dissociated on heating, and hence the liquid passing over remains moist. In the case of metallic sodium, phosphorus pentoxide and quicklime, the removal of the desiccating agent before distillation of the liquid is unnecessary, as the drying agent undergoes a chemical reaction with water to produce a stable, non-volatile product.

A very easy and efficient method of drying organic liquids and solutions of organic substances in suitable solvents is based on the principle of steam-distillation. Thus, when moist aniline is distilled (Expt. 4). at first a few drops of a turbid liquid, consisting of a mixture of aniline and water, pass over; and then follows a clear distillate consisting of pure dry aniline. Again, when a solution of a moist organic substance in benzene is distilled, the first few drops consist of a mixture of benzene and water, the mixture distilling at a temperature lower than the boiling point of pure benzene (80°C). After this, the benzene itself passes off, and the pure dry organic substance is left as a residue.

2 Methods of Testing the Purity of a Substance.

The following are the common methods for testing the purity of an organic substance:—

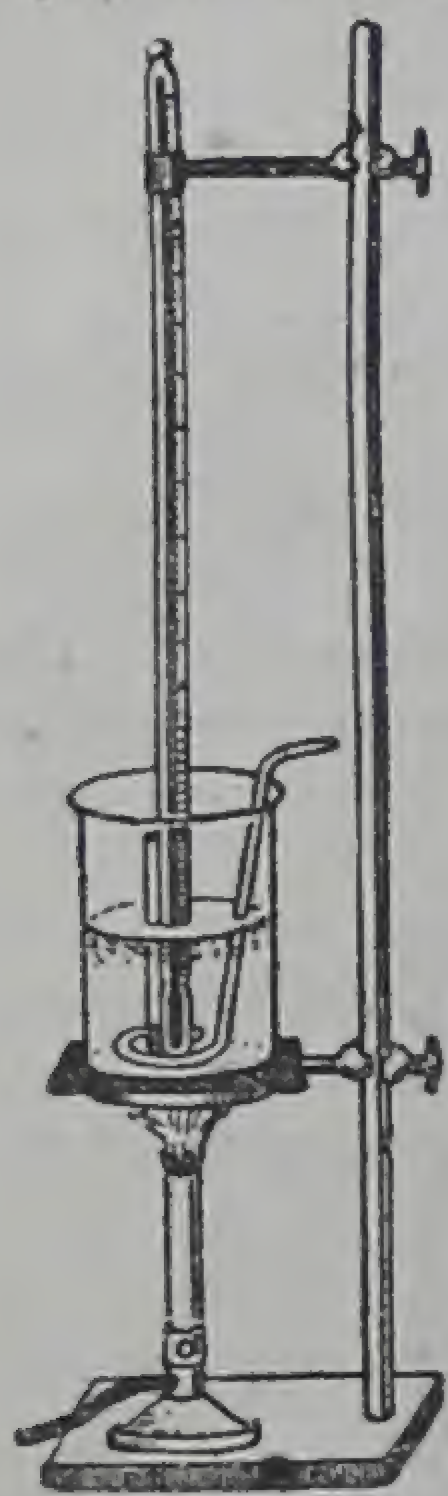
(1) **Melting Point.** The usual method for testing the purity of a solid organic substance is the determination of its melting point. This may be done in two different ways:—

(i) If a comparatively large amount of the substance is available, about 20 grams of it are carefully heated in a wide test-tube provided with a thermometer and a ring stirrer. When about three-quarter of the substance has melted, the burner is put out, and the liquid well stirred. The thermometer is read every half minute. The temperature at which the mercury column remains stationary for 2 to 3 minutes is taken as the melting-point of the substance.

Since the melting-point is defined as the temperature at which the liquid and the solid phases co-exist, it is absolutely necessary that *the solid and the liquefied substance are present and that the temperature remains constant for a pretty long period*. If the whole of the substance happens to melt, some more of the solid substance must be stirred in, and the lowest constant temperature reached should be noted.

Expt. 10. Using the apparatus described above determine the melting-point of naphthalene or ortho-nitrophenol.

(ii) In most cases, however, the quantity of the substance available



for the melting-point determination is small. For this reason, the usual method employed in chemical laboratories is as follows: A small quantity of the substance is finely powdered and introduced into a capillary tube, closed at one end. The capillary containing the substance is then moistened with concentrated sulphuric acid, and placed alongside a thermometer, suspended in a beaker containing concentrated sulphuric acid in such a way that (a) the substance in it is at the same level as the middle of the bulb of the thermometer, and (b) a part of it is within the liquid and the other part above it (Fig. 17). This latter arrangement makes the tube cling to the thermometer by capillary attraction.

The acid in the beaker is now heated with a small flame, and constantly stirred with a curved stirrer made of a thin glass rod, the substance and the thermometer being closely watched all the time. The *moment* the substance melts and becomes transparent, the temperature indicated on the thermometer is recorded. The experiment should be repeated, using a *fresh* tube and fresh substance.

Fig. 17.
Determination of
Melting-Point.

A pure solid has a perfectly definite and sharp melting point. Hence—

(i) If the given compound does not melt sharply, it should be taken as impure.

(ii) If the identity of the given compound is known, its melting-point is determined experimentally and compared with the true melting-point as given in a book of physical constants. If the two values agree, the given compound may be taken as pure. If, however, the melting-point of the compound is found to be lower, it is evidently impure.

(iii) If the identity of the compound is not known, the melting-point of the specimen is first determined. It is then recrystallized from a suitable solvent, and the melting-point determined once again.

If there occurs no change in the melting-point, the compound may be taken as pure. But if the second melting-point be higher than the first, the compound is impure.

Expt. 11. Using concentrated sulphuric acid or glycerine bath, determine the melting-point of urea (132°), iodoform (119°) or metadinitro-benzene (90°). Should the sulphuric acid of the bath turn dark during the experiment, it can be rendered colourless by adding a drop of concentrated nitric acid or a crystal of sodium nitrate.

(1) **Boiling Point.** In order to decide whether a given liquid is pure or impure, its boiling-point is determined by distilling it from a small distillation flask provided with a thermometer (Fig. 7, page 14). If the liquid is pure, the whole of it would distil at a constant temperature. If, on the other hand, the boiling-point rises during distillation, the liquid is impure.

For a correct boiling-point determination, the following points must be carefully attended to:—

(i) The bulb of the thermometer should be *wholly* surrounded by the vapour, *i.e.*, no part of it should dip into the liquid.

(ii) The vapour should not be allowed to get overheated; hence the size of the flame should be such that no part of it plays on that portion of the flask which contains the vapour.

(iii) The liquid should boil regularly, *i.e.*, without bumping. This is insured by adding one or two pieces of porous tile to the liquid before starting the distillation.

Siwolowoff's Method. The method described above requires a large quantity of the liquid. When only a small amount is available, the following method, due to Siwolowoff, may be used. The apparatus employed in this method is shown in Fig. 18. A few drops of the liquid under examination are placed in the small, thin-walled test-tube attached to the thermometer by means of a rubber band. A capillary tube, sealed about 1 cm. from the lower end, is placed in the test-tube which is then heated in a bath. At first air bubbles rise from the lower end of the capillary, due to expansion by heat, and these become more and more numerous as the temperature goes up. As soon as a rapid stream of bubbles of the vapour rises through the liquid, the burner is withdrawn from underneath the beaker, and temperature is noted at which the bubbles just cease to come out of the capillary.

Expt. 12. Determine the boiling-point of aniline (183°) or toluene (111°) by Siwolowoff's method.

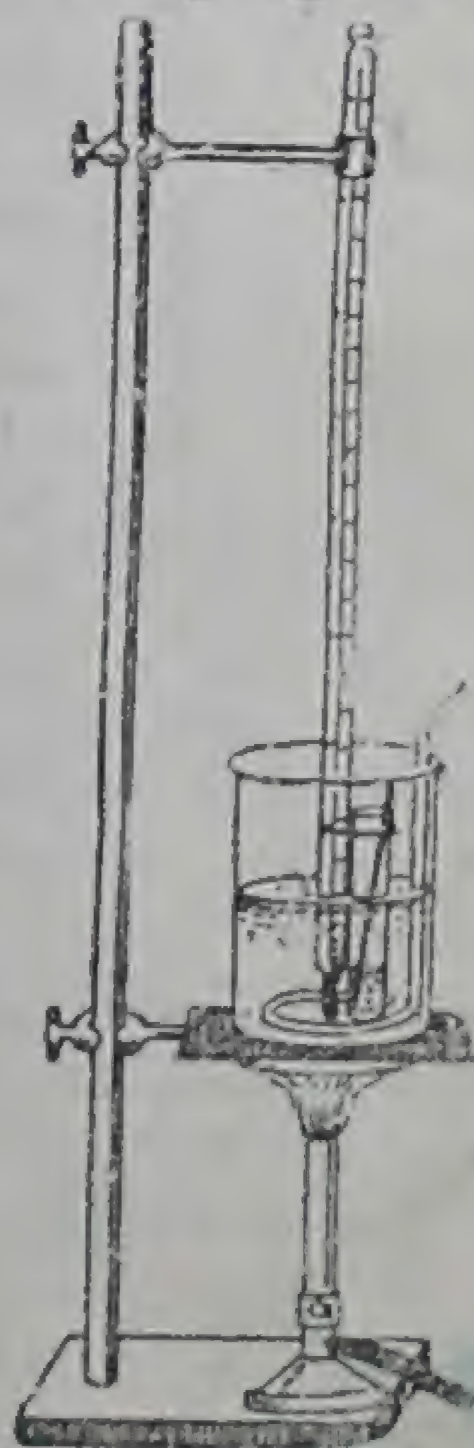


Fig. 18. Siwolowoff's Method for the boiling-point Determination

QUESTIONS

1. Write an account of the development of organic chemistry into a branch of science, indicating clearly the parts played by Scheele, Berzelius, Liebig, Lavoisier, Wöhler, Hennel, and Kekulé.

2. What considerations have led the chemist to separate Organic Chemistry from Inorganic chemistry?

3. Give a detailed account of the various methods used for the purification of organic compounds.

4. What do you understand by *fractional crystallization* and *fractional distillation*? Give instances of the use of these processes in practical organic chemistry.

5. Describe and explain the process of *steam distillation* and *distillation under reduced pressure*.

A mixture of nitrobenzene and water boils at 99°C under 760 mm. pressure. At this temperature the vapour pressure of water is 733 mm. What proportion of nitrobenzene will the distillate contain? (*Ans.* 20.1%)

6. Give an account of the usual methods employed for decolorizing organic substances containing small quantities of coloured impurities.

7. What are the different agents employed in the drying of organic liquids? Can they be used indiscriminately? Give illustrative examples to clear your point.

8. Give an account of the methods employed for testing the purity of organic compounds.

9. Describe how you would test the purity of an organic liquid. How would you effect the separation of a mixture of two liquids with boiling-points separated from each other, say by 10°C ? (*Punjab, Inter., 1930*)

CHAPTER II

QUALITATIVE ELEMENTARY ANALYSIS

3. General. Methods of systematic inorganic analysis are based almost entirely on ionic reactions, and consequently, it is always possible to analyse a mixture of two or more inorganic compounds without first separating it into the component substances. In the analysis of an organic substance, on the other hand, we have to depend on reactions that are essentially non-ionic, and liable to be affected considerably by the presence of other substances. For this reason, a mixture of organic substances must always be separated into its components before submitting it to qualitative and quantitative analyses.

The term "qualitative analysis", as used in organic chemistry, usually means the detection of various elements which are present in a given compound. The process is, therefore, often termed **qualitative elementary analysis**. It is a necessary step, in assigning a formula to every organic substance.

When the object is to establish the identity of an organic substance, *i.e.*, to prove that it is identical with some compound of known composition and properties, the process is called **identification**. A substance is usually identified by noting its appearance, smell, crystalline form, solubility, elementary composition and reactions, and finally by determining its melting or boiling-point. A very general method of testing the identity of two *solid* substances, *i.e.*, (1) the substance under examination, and (2) the compound with which it is supposed to be identical, consists in mixing a small quantity of each of the two samples and determining the melting-point of the mixture. If this is the same as the melting-point of the component solids, the identity of the two may be taken to be proved.

If the above methods fail to reveal the identity of the substance under examination, a qualitative elementary analysis, followed, if necessary, by a quantitative analysis, must be made. A complete identification of a compound may, at times, involve the determination of its molecular weight and a study of its chemical reactions.

4. Elements Occurring in Organic Compounds. Besides carbon, the most commonly occurring elements in organic

pounds are hydrogen, nitrogen, halogens and sulphur; less common are phosphorus, arsenic and metals.

5. Detection of Carbon and Hydrogen.¹

The only conclusive test for carbon and hydrogen is as follows: A small quantity of the pure, *dry* substance is mixed with 5 to 10 times its weight of freshly-ignited, powdered cupric oxide. The mixture is placed in a small, hard-glass test-tube and covered with a layer of cupric oxide. The test-tube is provided with a cork carrying a delivery-tube, the end of which is made to dip into some lime-water in another test-tube (Fig. 19). If the substance contains carbon, the latter is oxidized to carbon dioxide, which turns the lime-water milky. If it also contains hydrogen, small drops of water will collect in the cold part of the test-tube.

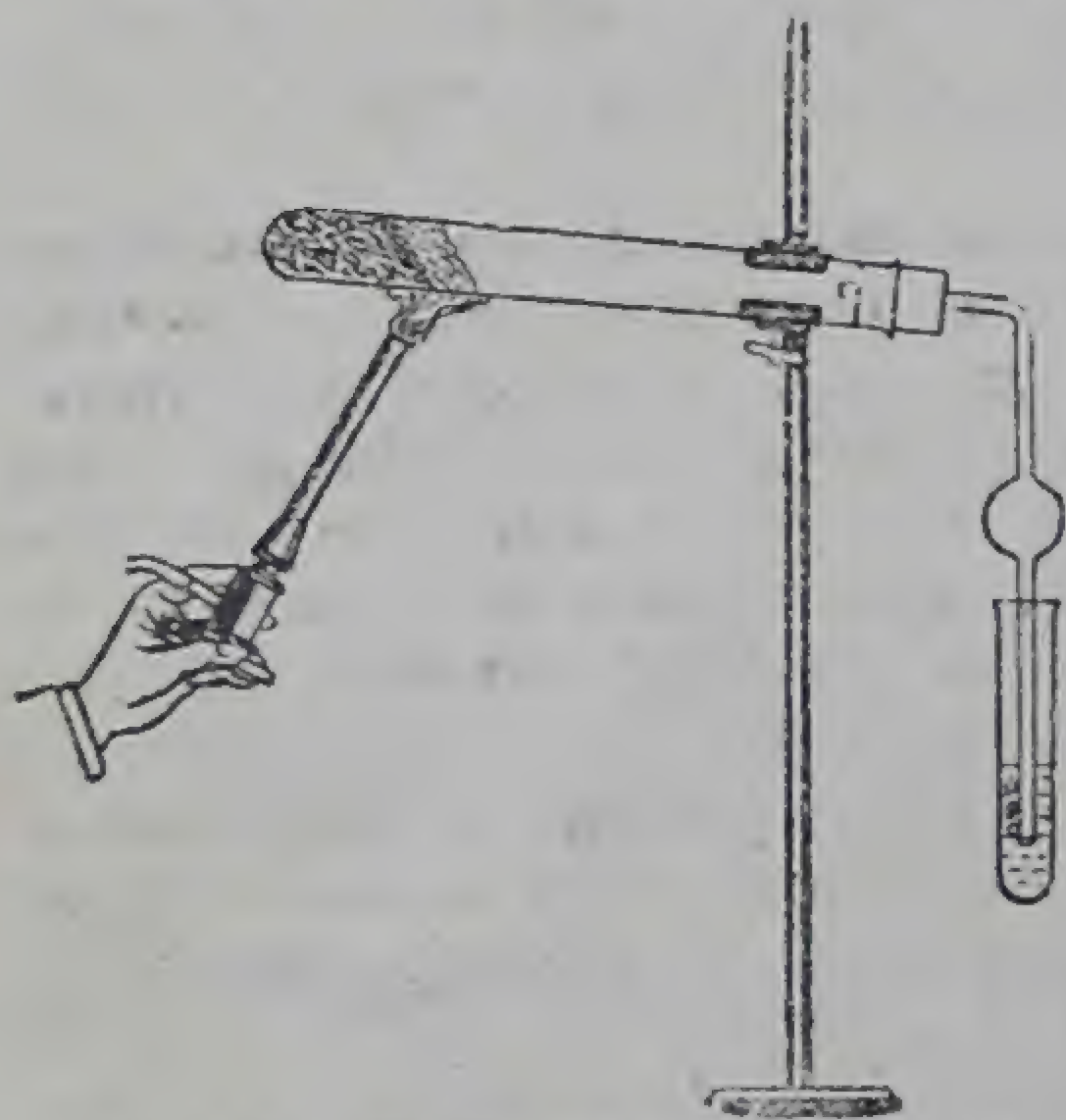


Fig. 19. Testing for Carbon and Hydrogen.

Expt. 13. By means of the apparatus given in Fig. 19 demonstrate the presence of carbon and hydrogen in urea.

6. Detection of Oxygen. There is no conclusive test for oxygen in an organic compound, though its presence may sometimes be inferred indirectly. Thus, if on heating the compound in a dry tube, drops of water condense on the upper, cool portion of the tube, the compound, obviously, must contain oxygen. Again, if the compound has been proved to be a carboxylic acid, alcohol, ether, aldehyde, carbohydrate, etc., it must contain oxygen.

The only sure way of proving the presence or absence of oxygen in an organic compound is by quantitative analysis. If the total percentage of the other elements present is less than 100, the difference is taken as the percentage of oxygen.

7. Detection of Nitrogen. (1) **Lassaigne's Test.** This is the most conclusive test for nitrogen. A freshly cut, small piece of sodium is melted in a hard-glass test-tube; a small amount of the substance is then added on to the molten metal, and the mixture is

¹ Many organic substances (*e.g.* starch, sugar, etc.) either char or burn with a smoky flame when heated on a platinum foil or in a porcelain crucible, owing to the liberation of free carbon.

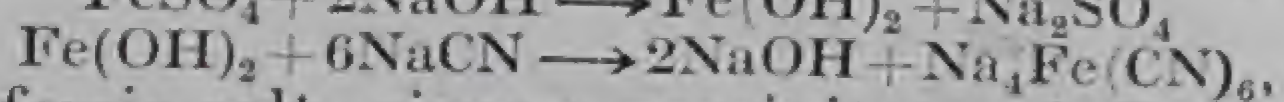
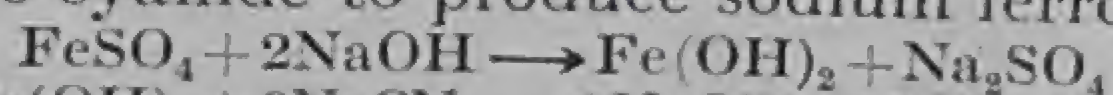
gradually raised to a red heat. Under these conditions, the nitrogen and the carbon of the compound combine with sodium to form sodium cyanide :



The tube, while still hot, is plunged into some distilled water in an evaporating basin. The liquid is boiled, filtered, and tested for the cyanide radical as follows :—

Its reaction towards litmus paper is first noted, which should be alkaline, owing to the formation of sodium hydroxide by the action of the water on the excess of sodium. The alkaline solution is warmed with a few drops of ferrous sulphate and a little ferric chloride, and then rendered acidic with concentrated hydrochloric acid. The formation of a blue precipitate, or a green coloration, proves the presence of cyanide in the solution, and therefore of nitrogen in the given organic compound.

The explanation of the above test for a cyanide is that ferrous hydroxide produced by the action of sodium hydroxide on the ferrous salt reacts with the cyanide to produce sodium ferrocyanide.



which, with the ferric salt, gives a precipitate of Prussian blue when the solution is acidified :—



When testing for nitrogen in a substance which also contains sulphur, we must use a much larger quantity of sodium than that employed ordinarily (for 0.02 gm. of the substance use 0.2 gm. sodium). This prevents the formation of sodium sulphocyanide.

When testing easily volatile substances for nitrogen, the heating must be very gradual and prolonged. Further, the tube employed must be much longer, so that the portion of the substance condensing in the upper, cold part of the tube flows back on to the heated sodium.

(2) **Evolution of Nitrogen.** Substances, such as the diazo-compounds, which lose nitrogen at moderate temperatures cannot be tested for this element by Lassaigne's method. In such a case, the substance is heated with cupric oxide in a test-tube filled with carbon dioxide and the evolved gas led into a long tube filled with potassium hydroxide solution. If nitrogen is present, the evolved gas is not wholly absorbed by potassium hydroxide.

(3) **Soda-lime Test.** In a comparatively small number of nitrogenous substances, the presence of nitrogen can be detected by heating the substance with soda-lime. If ammonia is evolved, the presence of nitrogen in the substance is proved. Should, however, the test be negative, it does *not* prove the absence of nitrogen. Nitro-compounds, for instance, do not respond to this test.

Expt. 14. Lassaigne's Test. Take a bright piece of sodium in a 2 inch test-tube of hard-glass and melt it. Add a *small* quantity of urea on to the molten metal. Heat the tube gradually, and finally raise the temperature to bright redness. Break the hot tube, in about 10 c.c. of distilled water contained in a dish. Stir up the liquid with a glass rod and filter. To the filtrate add a few drops of ferrous sulphate solution and a drop or two of ferric chloride. If the liquid be alkaline, a green precipitate of ferrous hydroxide will be produced at this stage. If no precipitate is formed, make the liquid alkaline with sodium hydroxide solution. Heat to boiling, and then acidify with hydrochloric acid. Formation of a blue precipitate or a green coloration, proves the presence of nitrogen in the substance.

Expt. 15. Soda-lime Test. Heat some urea or thiourea with soda-lime in a test-tube. Test the evolved gas for ammonia with litmus or turmeric paper. Show that no ammonia is evolved when dinitrobenzene is heated with soda-lime.

8. Detection of Sulphur. (1) Lassaigne's Test. This is applied in exactly the same manner as for nitrogen. The sulphur is converted into sodium sulphide, which is detected as given in Expt. 16.

(2) Oxidation to Sulphuric Acid. Easily volatile substances usually do not respond to Lassaigne's test. They are heated at 200 to 300°C with fuming nitric acid in a "bomb-tube" (see the quantitative estimation of sulphur, Chapter III). Under these conditions sulphur gets oxidized to sulphuric acid, the formation of which is detected by the barium chloride test.

Expt. 16. Fuse thiourea or sulphanilic acid with metallic sodium as in Expt. 14. Extract the fused mass with water, and filter. Test the filtrate as follows: (i) To a few drops of it add a freshly prepared solution of sodium nitroprusside; a transient, beautiful violet coloration. (ii) Place a drop of it on a silver coin; black stain of Ag_2S . (iii) Acidify a few drops with acetic acid and add lead acetate; a heavy black precipitate or a dark coloration.

9. Detection of Halogens. (1) Beilstein's Test. By means of this test the presence of a halogen in an organic substance can be detected very quickly and conveniently. A piece of copper wire is heated in the oxidizing flame, until it ceases to impart a green colour to the flame. It is then taken out of the flame, and a minute particle of the substance containing halogen is placed on it. The heating in the flame is repeated. At first a luminous flame may be produced owing to the burning of carbon. This is soon followed by a green or bluish green coloration, owing to the vaporization of the cupric halide.

Beilstein's test, though very simple and delicate, cannot be applied in the presence of acids and traces of metallic halides. It is also given by certain compounds containing no halogen, e.g. urea, a volatile cupric cyanide being produced in this particular case. Further, the test does not differentiate the halogens. In case of doubt, or when it

is desired to identify the halogen present, the following test is applied.

(2) **Lassaigne's Test.** In this test the substance is heated with sodium as in the detection of nitrogen. The fused mass is extracted with water and the solution filtered. The filtrate is strongly acidified with nitric acid and boiled so as to decompose the cyanide or sulphide, if present. Silver nitrate is then added; a precipitate of silver chloride (white), bromide (pale yellow) or iodide (yellow) shows the presence of chlorine, bromine or iodine in the substance under examination.

The necessity of boiling the filtrate with nitric acid arises out of the fact that if the substance contains nitrogen or sulphur, sodium cyanide or sulphide is formed. The former gives with silver nitrate a white precipitate and the latter a black precipitate.

Expt. 17. Beilstein's Test. Show by means of this test that cane-sugar contains no halogen. Also show that chloroform and dibromo-benzene contain halogen. Further, show that the test is positive when urea (a compound containing *no halogen*) is employed.

Expt. 18. Lassaigne's Test. By Lassaigne's test, show that chloroaniline (or quinine hydrochloride) contains a halogen: Note that the precipitate formed with silver nitrate is turned violet on exposure to light and is readily soluble in cold dilute ammonia. Hence, the halogen present is chlorine.

10. Detection of Phosphorus. The presence of phosphorus in an organic substance can be determined by heating it with (a) fuming nitric acid under pressure, (b) sodium peroxide, or (c) a mixture of sodium carbonate, and nitrate. The phosphorus is thus oxidized to phosphoric acid or sodium phosphate, which is tested with ammonium molybdate in the usual manner.

11. Detection of Metals. To identify the metal present in an organic substance, the latter is ignited on a piece of platinum foil. The residue is then examined for the common metallic radicals by the usual methods of inorganic analysis.

QUESTIONS

1. What do you understand by *elementary qualitative analysis* and *identification* of an organic compound? In what essential respects does qualitative organic analysis differ from qualitative inorganic analysis?

2. How would you know whether a given compound is organic or inorganic?

(Punjab, Inter., 1925)

3. How would you test an organic compound for the presence in it of (a) Hydrogen, (b) Nitrogen, (c) Sulphur, (d) Halogen, and (e) Oxygen?

(Punjab, Inter., 1928)

4. Describe with practical details the methods for the identification of:

(i) Nitrogen in an *unstable* organic substance.

(ii) Sulphur in a readily volatile organic compound.

(iii) Bromine in an organic substance that also contains nitrogen.

CHAPTER III

QUANTITATIVE ELEMENTARY ANALYSIS

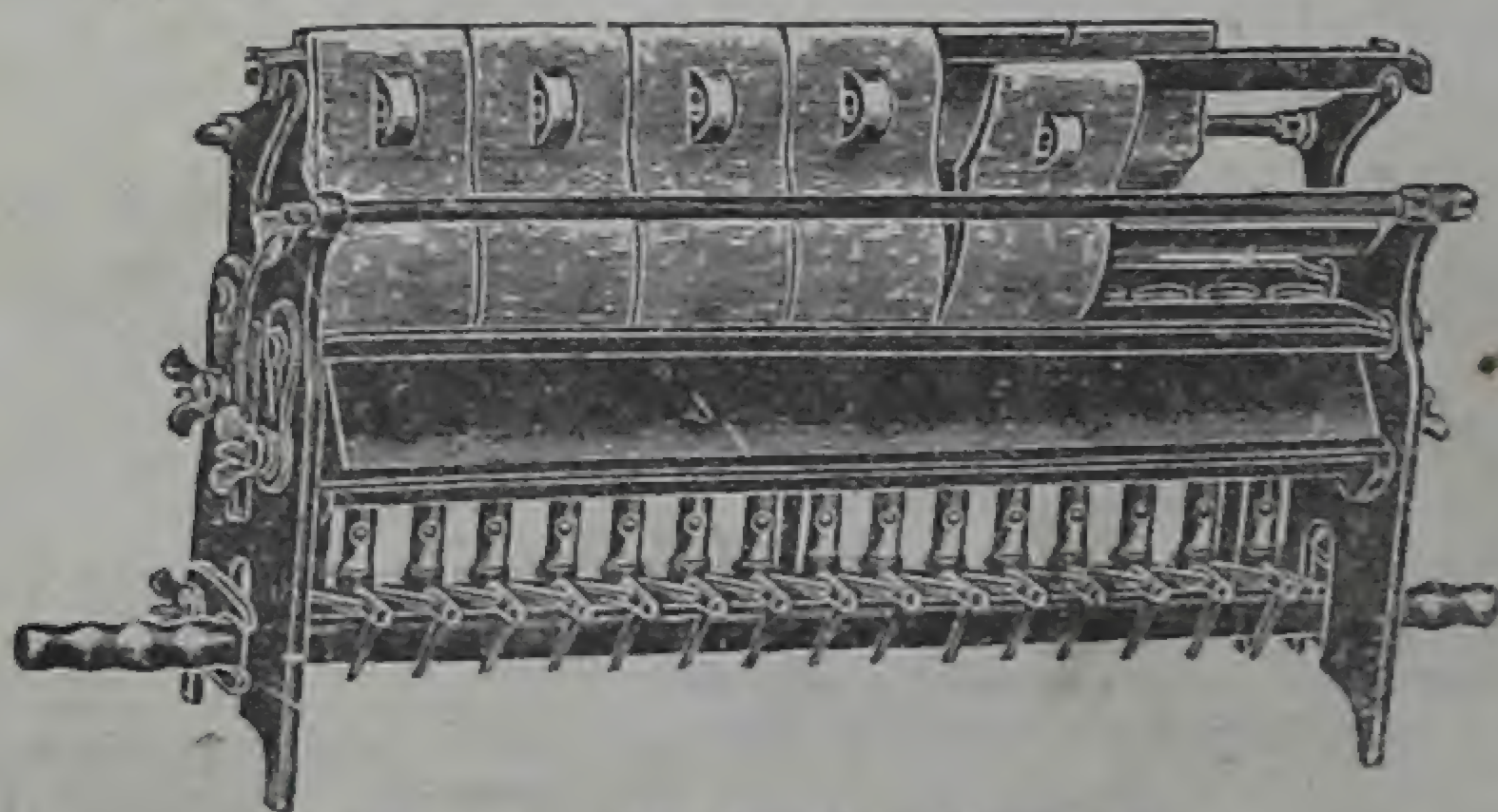
12. Estimation of Carbon and Hydrogen (Liebig's Method). Carbon and hydrogen are always estimated in one operation. The method employed consists in oxidizing, by means of cupric oxide, a known weight of the pure, dry substance and weighing the two products, namely, water and carbon dioxide. The process is known as Combustion, and is carried out in a current of dry oxygen or carbon dioxide-free air.

Apparatus. For the purpose of description it is convenient to divide the apparatus into the following three parts :—

(1) Apparatus for Delivering and Purifying Air and Oxygen. This consists of the following :—

- (i) Two reservoirs, one containing oxygen and the other air.
- (ii) Two towers, one containing solid potassium hydroxide and the other fused calcium chloride, connected to each of the reservoirs.
- (iii) A bubbler, which is a small bottle or bulb tube containing a few drops of concentrated sulphuric acid. This serves to show the rate at which the air or oxygen is passed through the apparatus.

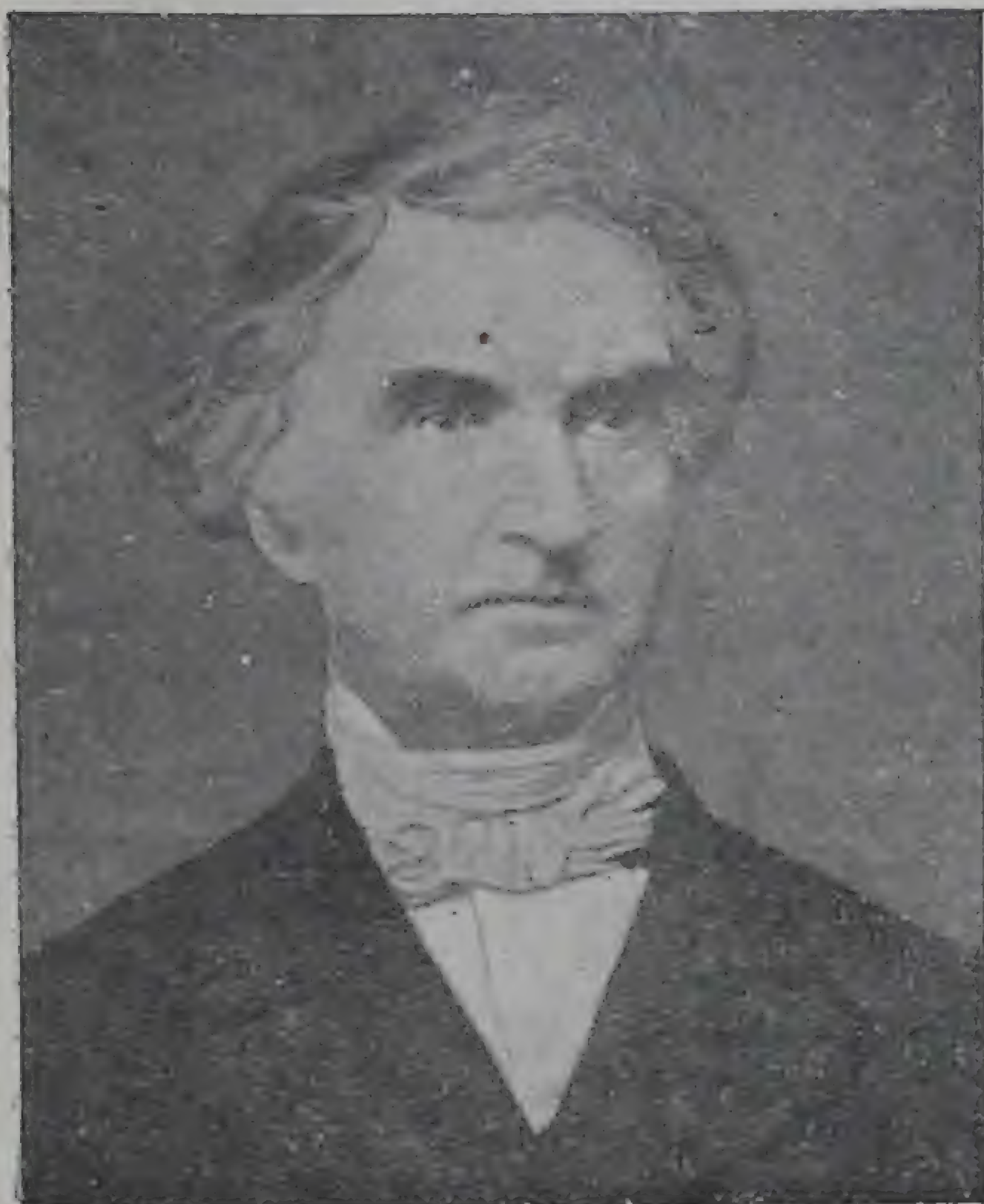
(2) Apparatus for Combustion. This consists of the following :



(i) A combustion furnace (Fig. 20), which is about 75 cm. long and has a row of burners, each provided with a tap, so that parts of the combustion tube could be heated as desired. Above the burners is a long iron tray, on which the combustion tube is placed

Fig. 20. Combustion Furnace.

and which serves to protect the tube from direct contact with the flames. The top of the furnace is provided with a number of tiles. These can be lowered over or raised from above the tube as desired, and thus serve to increase or decrease the intensity of heating.



JUSTUS VON LIEBIG

(1803—1873)

Liebig was born at Darmstadt, Germany, in 1803. He studied chemistry first at the German universities of Bonn and Erlangen, and then proceeded to Paris which was at that time the centre of chemical knowledge in Europe. He was fortunate enough to become the pupil of the Famous Chemist Gay-Lussac. In 1824 he returned to Germany, and at the young age of 21, was appointed Professor of Chemistry in the University of Giesse~~n~~. In 1852 he became Professor of Chemistry in the University of Munich, which post he continued to hold until his death in 1873.

Liebig invented the method of Quantitative Organic Analysis now in use. He investigated cyanates, cyanides, ferrocyanides, thiocyanates, and discovered hippuric acid, chloral, chloroform, aldehyde, benzil, and elucidated the constitution of organic acids and amides. In collaboration

with Wohler he carried out researches on uric acid and its derivatives.

(ii) *The Combustion Tube.* This is a hard-glass tube open at both ends, and is about 10 cm. longer than the furnace. It is first cleaned

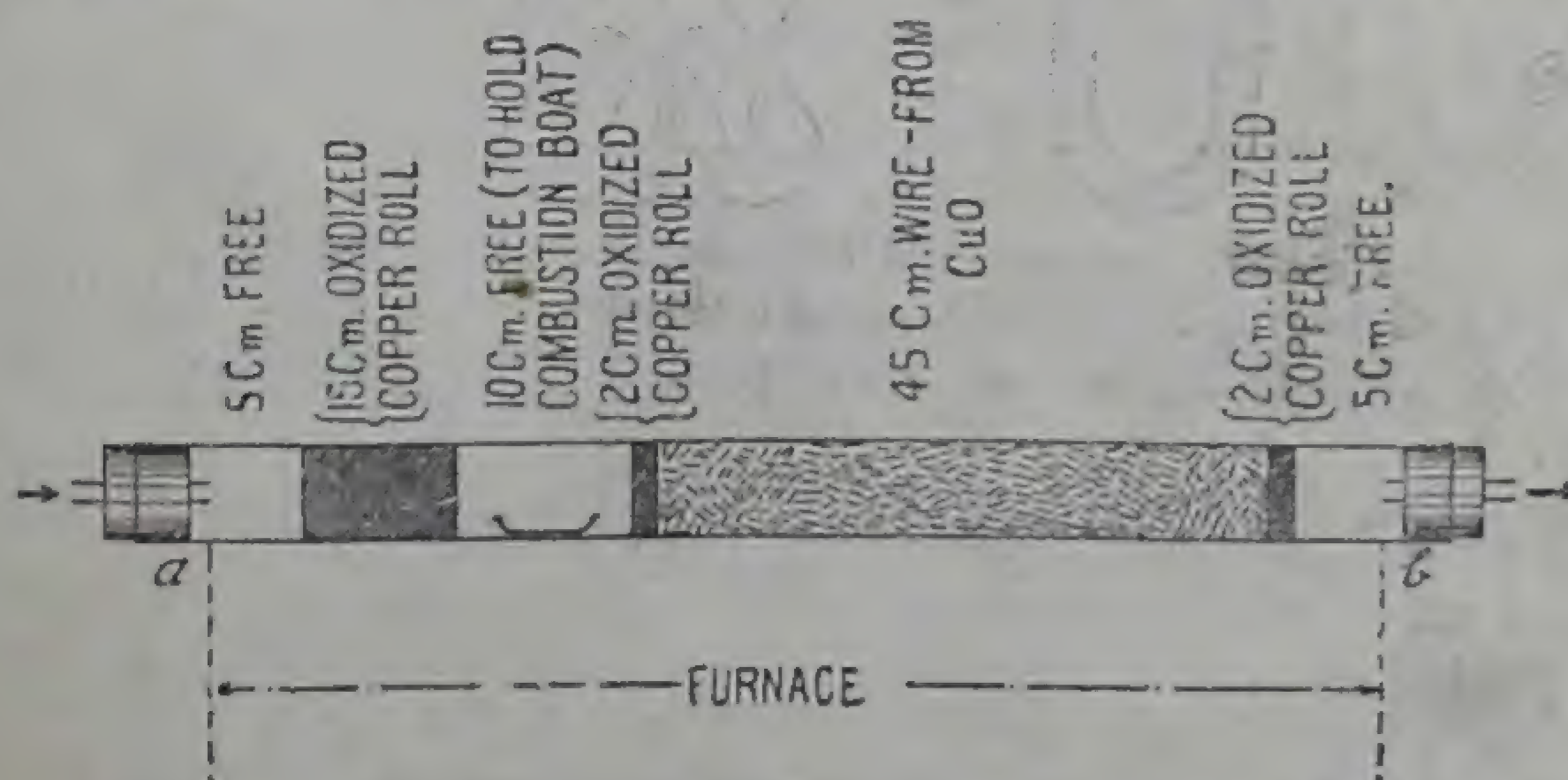


Fig. 21. Method of filling the Combustion Tube.

and dried and then filled with dry, ignited, wire-form cupric oxide, to a length of 45 cm. (as shown in Fig. 21), the cupric oxide being

kept in position by a short, tightly-fitting roll of copper gauze. The 15 cm. copper roll is also put into position as in the figure, while the space (10 cm.) meant for the boat is kept free.

(3) Apparatus for Collecting and Weighing the Water and Carbon Dioxide. This is shown in Fig. 22 and consists of :--

(i) A calcium chloride U-tube, provided with a trap at the side. The greater part of the water produced during the combustion collects in the trap, while the rest is absorbed by the calcium chloride. Nowadays, there is a tendency to using pumice-stone soaked in concentrated sulphuric acid instead of fused calcium chloride.

(ii) Potash bulbs, three-fourth filled with concentrated potassium hydroxide solution (1 : 1.5). This is effected by dipping the end *a* into the solution and *gently* sucking at the end *b* by means of a piece of rubber tubing, an empty wash-bottle being interposed between the mouth and the potash bulbs to prevent the passage of the liquid into the mouth. Attached to the bulbs is a horizontal tube, *c*, which is filled with small pieces of solid potassium hydroxide. The latter serves to catch moisture carried away by the gas during its passage through the potassium hydroxide solution, and, further, retains any carbon dioxide that might escape absorption in the bulbs. Soda-lime is sometimes preferred to aqueous potassium hydroxide, as it absorbs carbon dioxide more quickly.

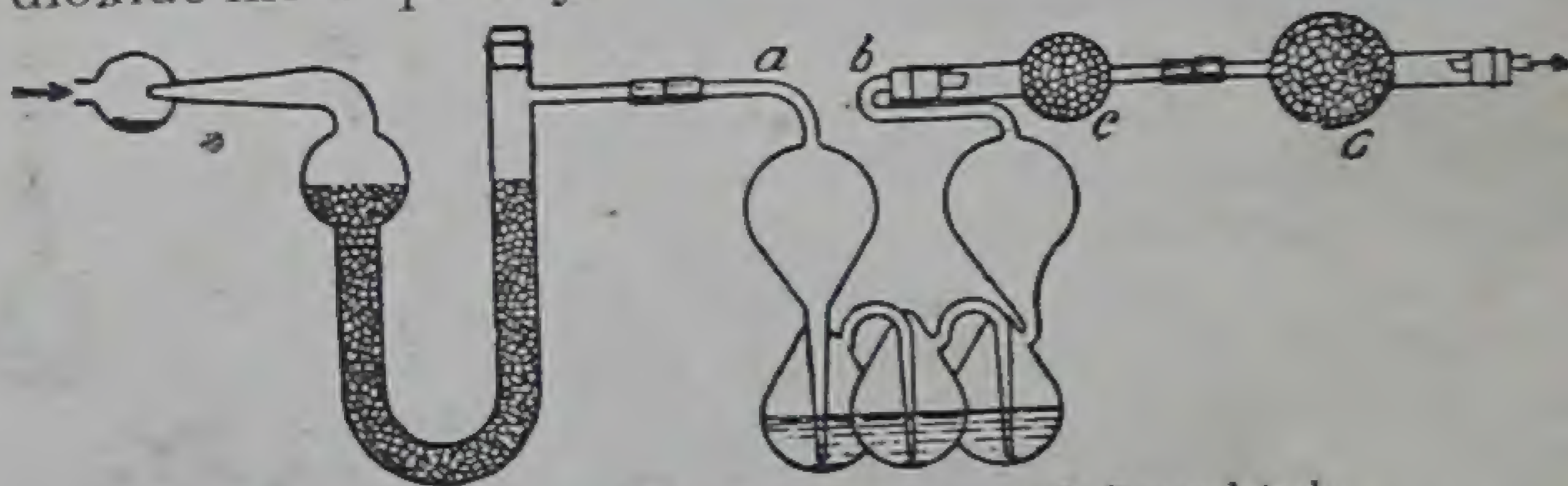


Fig. 22. Absorption Apparatus and Guard tube.

(ii) A guard tube, *G*, containing calcium chloride, which serves to protect the side-tube, *c*, of the potash bulbs from atmospheric moisture.

The complete set-up of apparatus for the estimation of carbon and hydrogen is shown in Fig. 23.

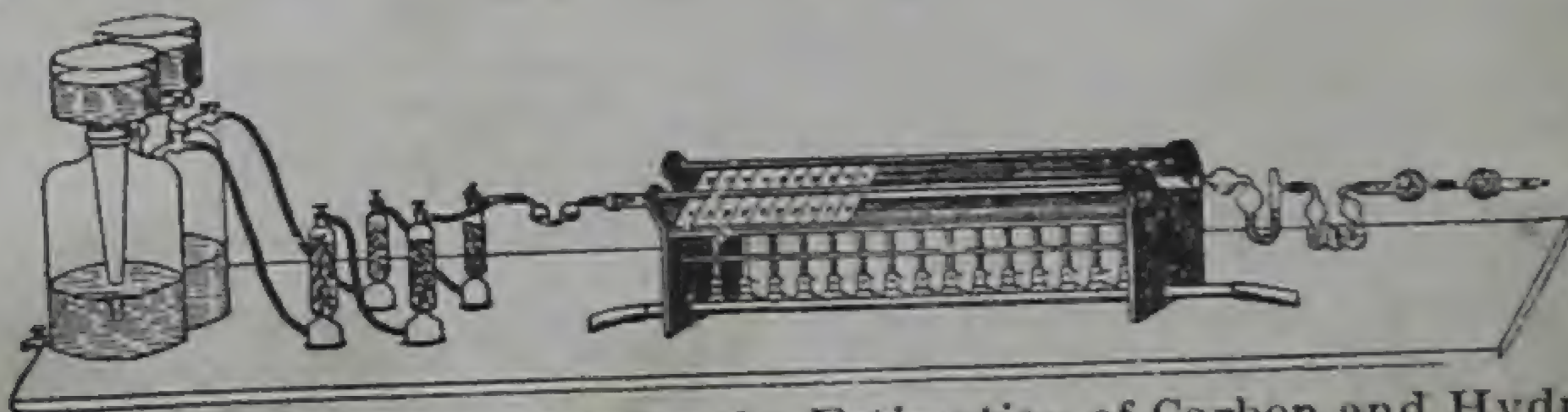


Fig. 23. Complete Apparatus for the Estimation of Carbon and Hydrogen.

Procedure. The procedure may be divided into three stages :—

(1) **Igniting the Cupric Oxide.** Before introducing the substances to be analysed and making a connection with the absorption apparatus, it is absolutely necessary to ignite the cupric oxide. This is brought about by gradually lighting all the burners beneath the combustion tube, and passing a slow current of pure dry air through it. The water that may condense at the forward, cool end, *b*, of the tube is removed with a piece of filter paper wrapped round a glass rod. When no more moisture collects, the front end, *b*, of the tube is closed with a rubber bung carrying a calcium chloride tube. After about half an hour's heating the burners under the oxidized copper roll, the adjacent empty space, and about 5 cm. of the wire-form cupric oxide layer that lies next, are put out, and the current of air stopped.

(2) **Weighing the Substance and the Absorption Apparatus.** While the rear part of the tube is cooling, the substance to be analysed (about 0.2 gm.) and the two absorption vessels are weighed. The substance, unless volatile, is weighed in a porcelain boat (Fig. 24, *A*) which has previously been ignited and cooled in a desiccator, A volatile liquid must be weighed in a small stoppered tube (Fig. 24, *B*) or in bulb tube (Fig. 24, *C*) which is sealed before weighing.

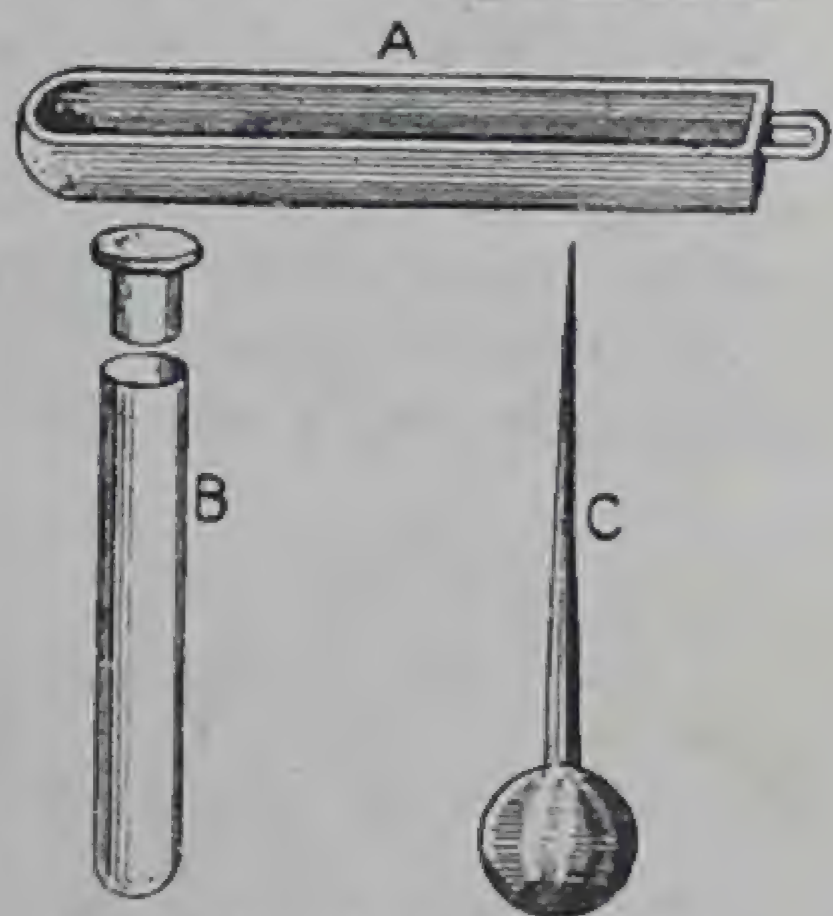


Fig. 24. Apparatus for Weighing the Substance.

(3) **Combustion.** When the rear end, *a*, of the combustion tube has cooled, the oxidized copper roll is taken out with a wire, the boat containing the weighed amount of the substance is introduced, the roll placed, and the connection of the combustion tube with the purifying apparatus and the absorption apparatus made. In the case of a volatile liquid, the sealed off end is filed and broken off. The bulb is then placed in the boat with its open end raised and directed towards the cupric oxide layer.

A slow current of oxygen (2 bubbles per second) is now admitted to the tube. Flames under the oxidized copper roll are just lighted, and their size gradually increased, until, finally, the spiral is brought to a dull red heat. Next, the burners under the unheated cupric oxide are gradually lighted, great care being taken not to allow any flame near the boat to become too large.

Now comes the most difficult part of the procedure, upon which depends the success of the analysis, namely *very gradual* heating of the

substance. The heating must be started with a single small flame, which is gradually lighted. Next the tiles on one side of the tube are put on, and then on the other. Finally the flames are turned full. In the case of a readily volatile substance, the heating should not be started with the flame, but by covering the part of the combustion tube containing the boat with hot tiles taken from the heated front portion of the furnace.

When the burners under the boat have been burning full for about 20 minutes the combustion is regarded as being over. Any moisture that might condense near the ends of the tube is driven over into the absorption apparatus by heating with a small flame or better by a hot tile. In order to completely sweep out the products of combustion into the absorption apparatus, the rate of the passage of oxygen is somewhat increased. Finally the oxygen in the absorption apparatus is replaced by air,¹ and after allowing to cool to the room temperature, the calcium chloride tube and the potash bulb are weighed. The increase of weight in the two cases gives, respectively, the amount of water and carbon dioxide produced during the combustion.

Example. On combustion, 0.210 gm. of glucose gave 0.307 gm. of carbon dioxide and 0.127 gm. of water. What is the percentage of carbon and of hydrogen in the compound?

$$\text{Wt. of carbon in } 0.307 \text{ gm. of } \text{CO}_2 = 0.307 \times \frac{12}{44} \text{ gm.}$$

$$\therefore \text{Percentage of carbon} = 0.307 \times \frac{12}{44} \times \frac{100}{0.210} = 39.9$$

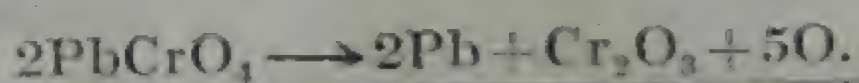
$$\text{Wt. of hydrogen in } 0.127 \text{ gm. of } \text{H}_2\text{O} = 0.127 \times \frac{2}{18} \text{ gm.}$$

$$\therefore \text{Percentage of hydrogen} = 0.127 \times \frac{2}{18} \times \frac{100}{0.210} = 6.7.$$

13. Estimation of Carbon and Hydrogen in the presence of Nitrogen, Halogens, Sulphur or Phosphorus. When the substance contains *nitrogen* a freshly reduced coil of copper gauze is placed in the extreme front part of the combustion tube. This serves to reduce the acidic oxides of nitrogen which would otherwise be absorbed by potassium hydroxide in the bulbs.

When the substance contains a *halogen* but no sulphur, a coil of silver gauze is used. This is kept cool, and serves to decompose the volatile halides of copper that may be produced during the combustion.

In analysing a substance containing a *halogen, sulphur, or phosphorus*, the usual practice is to use lumps of fused lead chromate instead of cupric oxide. Lead chromate acts as a powerful oxidizing agent at high temperatures:—



¹ If this is not done the apparent weight of the absorption apparatus will be more than its actual weight.

It has a distinct advantage over cupric oxide, as the salts of lead (namely the halides, the sulphate, and the phosphate) are far less volatile and much more stable than the corresponding salts of copper.

14. Dennstedt's Method. This method was introduced in 1906, and is now employed in many laboratories. It has an advantage over Liebig's method in that no combustion furnace is required and a great saving of gas is effected. The principle underlying this method consists in passing a mixture of oxygen and the vaporized substance over a catalyst, consisting of platinum, platinized quartz, or platinized asbestos. Water and carbon dioxide are caught in weighed tubes containing calcium chloride and soda-lime respectively,

In case the substance under examination contains *nitrogen* or *sulphur*, it yields, in addition, NO_2 in the former case and a mixture of SO_2 and SO_3 in the latter. Before being admitted into the absorption apparatus, the gases are passed over heated lead dioxide, which absorbs NO_2 , forming lead nitrate, and also SO_2 , and SO_3 , forming lead sulphate. The last named substance can be separated and weighed. Thus it is possible to estimate carbon, hydrogen and sulphur in one operation.

If the organic substance contains both nitrogen and halogen (*e.g.* substituted quaternary ammonium and azonium halides) the products of combustion are passed over heated silver spiral (or molecular silver) contained in a porcelain boat, placed in the front part of the tube. The oxides of nitrogen are thus reduced to free nitrogen which escape. The halogen is retained by silver. The gain in weight of the porcelain boat gives the weight of the halogen. Carbon, hydrogen and halogen are estimated in one operation in this way.

15. Estimation of Oxygen. There is no direct method for the estimation of this element. Its amount in an organic substance is always found by *difference* (Sec. 6).

16. Estimation of Nitrogen. There are two different methods in general use for the estimation of this element:—

(1) **Dumas' Method.** This method consists in "combusting" the substance with cupric oxide in a current of carbon dioxide, decomposing any oxides of nitrogen formed, by passing the gases over a heated spiral of metallic copper, and collecting the nitrogen over a strong solution of potassium hydroxide. The apparatus employed is shown in Fig. 25. It consists of: (i) a combustion tube open at both ends, and about 10 cm. longer than the bed of the combustion furnace to be used, (ii) CO_2 generator which generally consists of hard-glass tube charged with sodium bicarbonate, (iii) a nitrometer, which consists of a graduated glass tube, provided at the top with a funnel and a tap, and at the base with a mercury trap and a levelling bulb, and

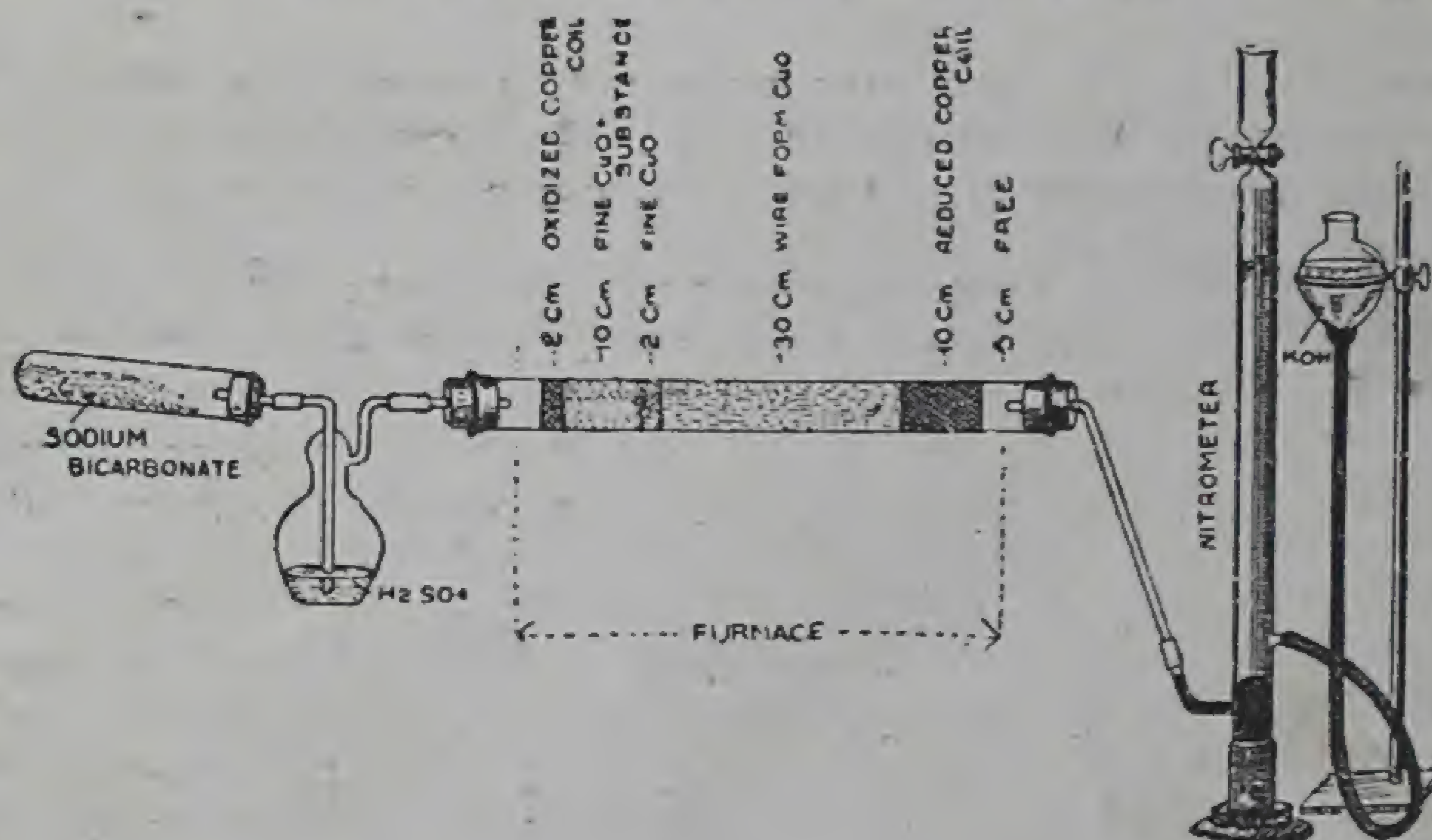


Fig. 25. Estimation of Nitrogen by Dumas' Method.

Dumas was born on July, 14 1800, at Alais, France. He discovered the well-known method for the *estimation of nitrogen* in an organic substance and also a method for the determination of *vapour densities*. He investigated the nature of *oxamides* and of *ethyl oxamate*, isolated *methyl alcohol* and established the *doctrine of homology*. Dumas was an admirable speaker, and possessed rare literary gifts. He exercised great influence in scientific and academic circles in France.



JEAN BAPTISTE ANDRE DUMAS
(1800—1884)

(iv) a "bubbler," i.e., a small size gas-washing bottle containing some concentrated sulphuric acid which is interposed between the CO_2 generator and the combustion tube, and serves to show the rate at which the gas is passing.

The nitrometer is charged with a 50 per cent solution of potassium hydroxide, and the combustion tube is filled as shown in the figure. A weighed amount of the substance is intimately mixed with fine cupric oxide, and the mixture is introduced into the tube through a funnel. The mortar is rinsed out several times with small quantities of fine cupric oxide, and the rinsings also introduced into the tube. The weight of the substance taken should be sufficient to give 30 to 40 c.c. of nitrogen. The copper coil in the front end of the tube is reduced by heating it strongly in a blowpipe flame and dropping it into a test-tube containing a few drops of methyl alcohol, which is then removed by placing the coil under reduced pressure. Before being used, cupric oxide should be strongly ignited, in order to remove all organic nitrogenous matter. The coil in the back end of the tube is oxidized by strongly igniting it in air.

After being properly filled, the tube is placed in the furnace and connected to the CO_2 generator and the nitrometer. The solution in the nitrometer is run out by opening the tap and lowering the leveling bulb. The tube containing sodium bicarbonate is now heated to obtain a fairly rapid current of carbon dioxide, which drives the air out of the apparatus. The issuing gas is tested from time to time by filling the nitrometer with potassium hydroxide solution. When the air in the apparatus has been completely expelled, as shown by the gas bubbles being completely absorbed by the alkali solution in the nitrometer, the latter is completely filled with potassium hydroxide solution, and the heating of the combustion tube started as follows:— First the burners are lighted from the nitrometer end to about 6 inches of the substance. When this part of the tube is at a dull red heat, the heating is commenced from the other end, and gradually extended towards the substance. At this stage, the passage of carbon dioxide will have to be slowed down. The heating of the bicarbonate and of the substance should be so controlled that the gas enters into the nitrometer in a regular stream (about 2 bubbles per second). Towards the end, the stream of carbon dioxide will, of course, have to be again increased. When the gas bubbles are being, once again, completely absorbed, the combustion may be taken to be over. The nitrometer is now disconnected, the gas is allowed to cool down to the room temperature, and its volume recorded. After reading the barometer, the volume is reduced to N.T.P. The tension of 50 per cent potassium hydroxide solution at the room temperature may be either read from the table, or taken to be approximately two-third

that of the water vapour at the same temperature. From the volume of nitrogen corrected to N.T.P. its percentage by weight is calculated.

Example 2. *0.188 gm. of an organic compound gave, on combustion, 31.8 c.c. of moist nitrogen measured at 14°C and 758 mm. pressure. What is the percentage of nitrogen in the compound? Aqueous tension at 14°C = 12 mm.)*

Volume of dry nitrogen reduced to N.T.P.

$$= 31.8 \times \frac{273}{273 + 14} \times \frac{758 - 12}{760} \text{ c.c.} = 29.7 \text{ c.c.}$$

Now, 22.4 litres of Nitrogen at N.T.P. weigh 28 grams.

∴ Weight of 29.7 c.c. of nitrogen at N.T.P.

$$= 28 \times \frac{29.7}{22.4 \times 1000} = 0.0371 \text{ gm.}$$

Percentage of nitrogen in the compound

$$= 0.0371 \times \frac{100}{0.188} = 19.7.$$

(2) **Kjeldahl's Method.** This method consists in heating the substance with concentrated sulphuric acid and potassium sulphate. The latter serves to raise the boiling point of the liquid and thus facilitates the oxidation of the substance by sulphuric acid. A small quantity of mercury, mercuric oxide, manganese dioxide, or cupric sulphate is also added to facilitate oxidation. Carbon and hydrogen of the substance get oxidized to water and carbon dioxide respectively, while the nitrogen is converted into ammonia, which combines with the excess of the acid present to form ammonium sulphate. After the reaction is over, the mixture is distilled with an excess of sodium hydroxide solution and the ammonia set free is estimated by absorbing it in a measured excess of standard acid.

The method gives good results with amines, ammonium compounds, amino-acids, proteins and related compounds, pyridine and quinoline derivatives, and alkaloids. It is employed particularly in agricultural laboratories for the analysis of food-stuffs, manures and other products. In analysing nitro-, azo- or azoxy-compounds and nitrates, or nitrites, the substance must be reduced before submitting the same to kjeldahlizing.

An accurately weighed quantity (about 0.5 gm.) of the finely powdered substance, together with about 20 c.c. of pure concentrated sulphuric acid, about 10 gm. of anhydrous potassium sulphate and a small crystal of copper sulphate, is heated in a Kjeldahl flask (Fig. 26A). Since large quantities of sulphur dioxide are evolved, the heating must be conducted in a fume closet. The completion of the process is indicated by the reaction mixture (which first turns very dark) becoming clear and colourless.

The reaction mixture, after it has cooled somewhat, is transferred together with rinsings, to a round-bottom flask provided with a tap-funnel and connected, through a trap and a vertical condenser, with a conical flask containing a measured volume (50 c.c.) of $N/10$ H_2SO_4 (See Fig. 26 *B*). An excess of caustic soda solution (40 grams of $NaOH$ in 100 c.c. of water) is run in from the tap-funnel, and the mixture boiled for about half an hour. At the end of this time, the excess of the acid in the conical flask is titrated with $N/10$ sodium hydroxide, using methyl orange as indicator.

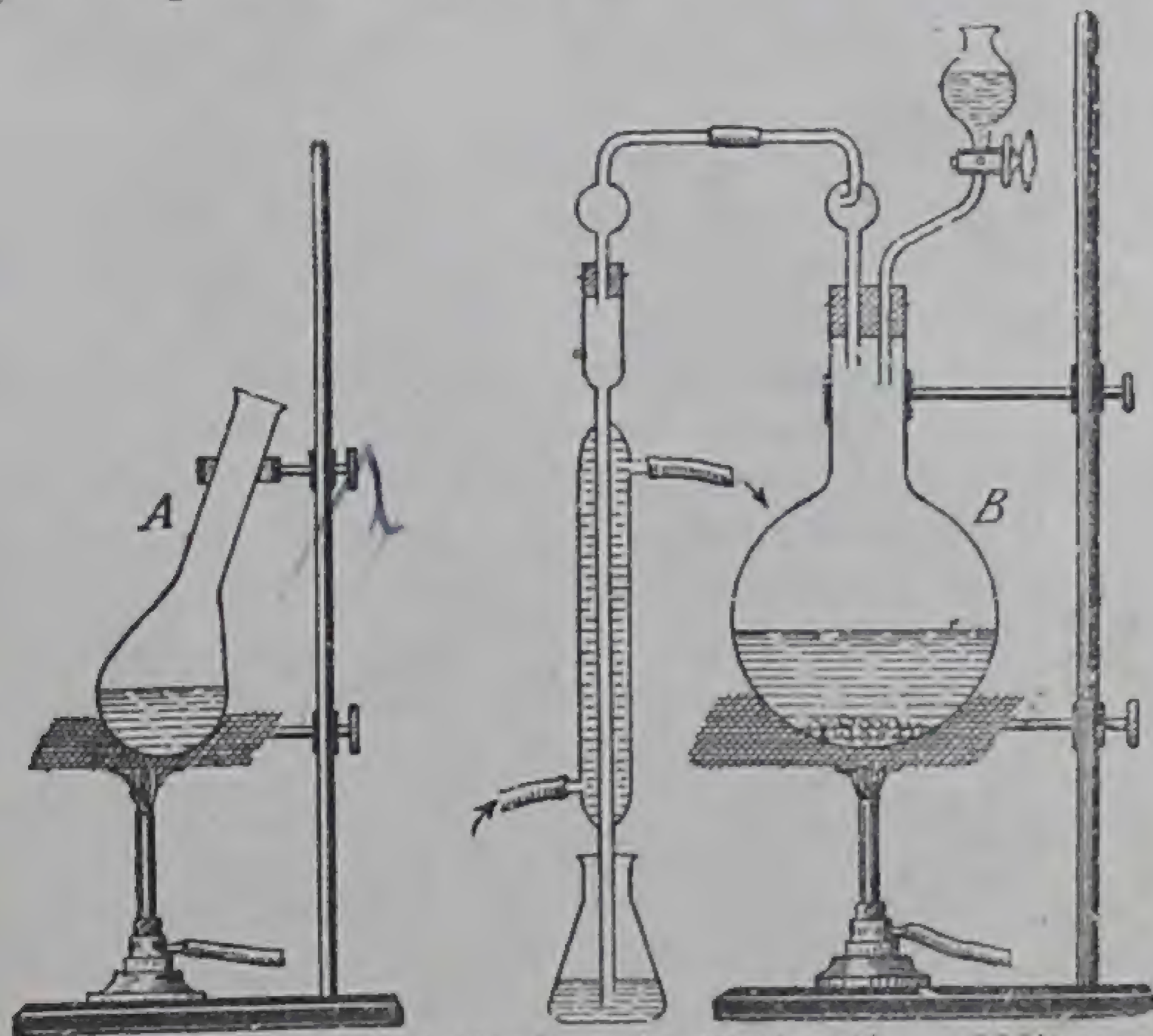


Fig. 26. Kjeldahl's Method of the Estimation of Nitrogen.

Expt. 19. Find the percentage of nitrogen in acetanilide by Kjeldahl's method. Use about half a gram of the substance, and proceed as described above.

Example 3. In a Kjeldahl nitrogen estimation the ammonia resulting from 0.442 gm. of the substance was distilled into 50 c.c. of $N/10$ H_2SO_4 . The excess of the acid required 14.0 c.c. of $N/10$ $NaOH$. Calculate the percentage of nitrogen in the substance.

14.0 c.c. of $N/10$ $NaOH$ are equivalent to 14.0 c.c. of $N/10$ H_2SO_4 .

\therefore Volume of $N/10$ H_2SO_4 neutralized by ammonia that is evolved
 $= 50 - 14.0 \text{ c.c.} = 36.0 \text{ c.c.}$

36 c.c. of $N/10$ $H_2SO_4 \equiv 36 \text{ c.c. of } N/10 \text{ } NH_4OH$

Now, the amount of combined nitrogen contained in 1 litre of normal $NH_4OH = 14 \text{ gm.}$

\therefore Amount of nitrogen contained in 36 c.c. of $N/10$ NH_4OH

$$= 14 \times \frac{36}{1000} \times \frac{1}{10} \text{ gm.} = 0.0504 \text{ gm.}$$

Hence the percentage of nitrogen in the substance

$$= 0.0504 \times \frac{100}{0.442} \text{ per cent} = 11.4 \text{ per cent.}$$

17. Estimation of Halogens. (1) Carius' Method. The

estimation of a halogen by this method is carried out by heating the substance with fuming nitric acid in the presence of a few crystals of silver nitrate in a sealed tube. Carbon and hydrogen are oxidized to carbon dioxide and water, while the halogen forms silver halide, which is collected, washed, dried, and weighed.

The estimation is carried out in a "bomb tube"—a special Jena glass tube with thick walls to withstand pressure. About half a gram of powdered silver nitrate and about 4 c.c. of pure, fuming nitric acid (sp. gr. 1.5) are placed in the tube, and then a small narrow test-tube containing an accurately weighed quantity (about 0.2 gm.) of the substance is allowed to slide down into the inclined bomb tube. The test-tube will stand in the acid with its open end clear (Fig. 27). The upper end of the bomb tube is then carefully sealed off, and the tube is wrapped in asbestos paper and heated in a bomb furnace (Fig. 28) at 150—200°C for about 6 hours.

Fig. 27. Carius' Tube.

When the furnace has cooled down, the capillary end of the tube is carefully opened, and the contents washed out into a beaker by means of distilled water. The precipitate of silver halide is separated, dried and weighed.

Example 4. 0.369 gm. of a substance gave 0.568 gm. of AgBr. Find the percentage of bromine in the substance.

Since 188 parts by weight of AgBr contain 80 parts of bromine, the quantity of bromine in 0.568 gm. of AgBr

$$= 0.568 \times \frac{80}{188} \text{ gm.}$$

Hence, the percentage of bromine in the substance

$$= 0.568 \times \frac{80}{188} \times \frac{100}{0.369} = 65.5.$$

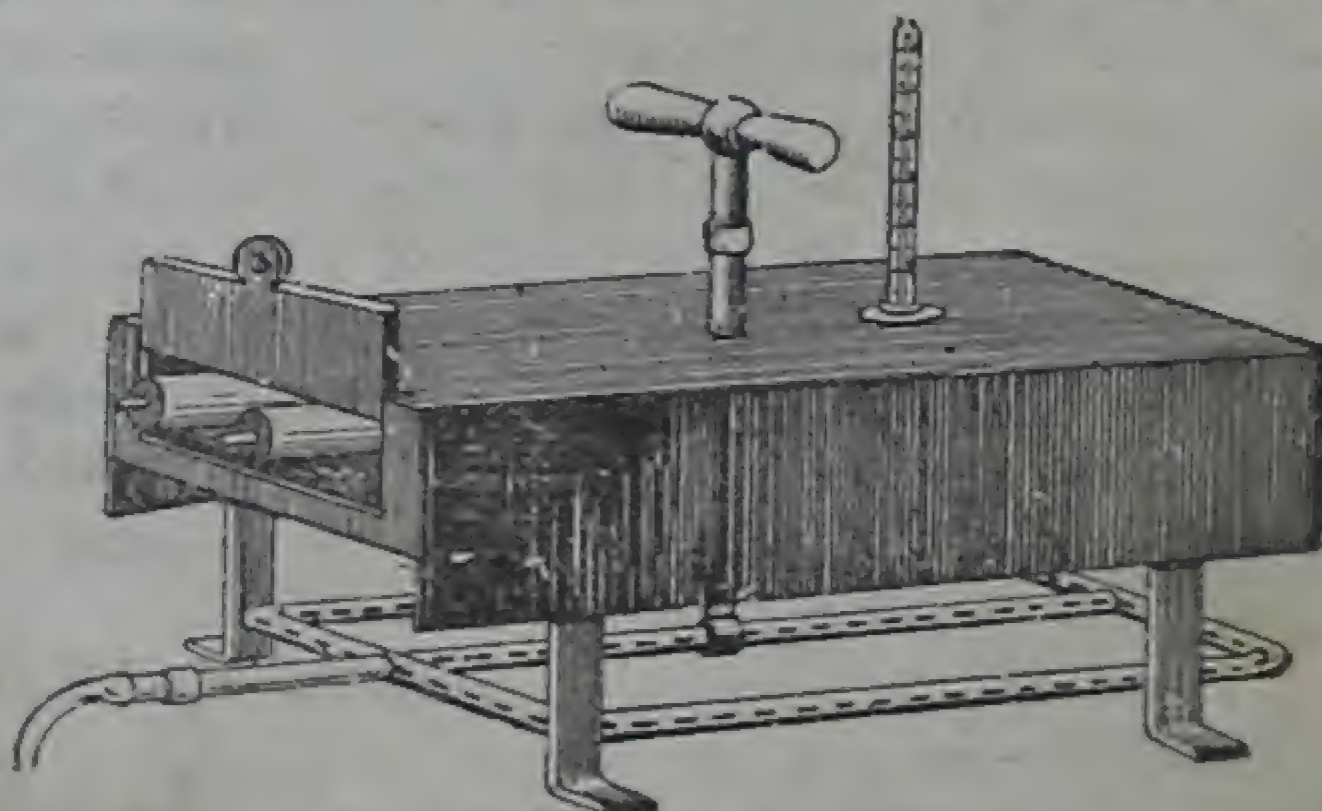
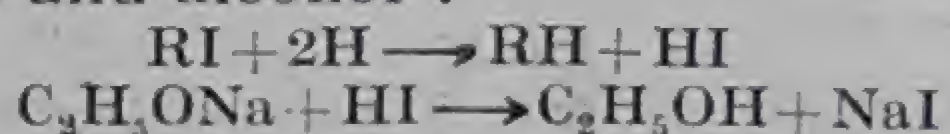


Fig. 28. Bomb Furnace.

(2) **Stepanow's Method.** The Carius' method has certain drawbacks. Owing to high pressures developed in the tube, explosions may sometimes occur. Further, the method does not give good results with compounds containing iodine partly on account of the solubility of silver iodide in nitric acid and partly on account of the liberation of free iodine. Other methods have, for these reasons, been devised for the estimation of halogens. One of these is that of Stepanow, which is not only easier in manipulation but also gives quite reliable results even in the case of iodine compounds.

A known weight of the substance is boiled with 98 per cent alcohol under a reflux condenser, and an excess of sodium metal is gradually added. Thus hydrogen and sodium alcoholate are formed. The halogen of the compound gets replaced by hydrogen, and the halogen hydracid produced at the same time reacts with sodium alcoholate to yield sodium halide and alcohol.



After distilling off the alcohol, the residue is acidified with nitric acid and the halide estimated volumetrically by Vohlard's method.

18. Estimation of Sulphur and Phosphorus. (Carius' Method). The estimation of these two elements is carried out in a manner similar to that employed in the case of halogens, but without the addition of silver nitrate. Sulphur and phosphorus get oxidized to sulphuric and phosphoric acids respectively. These are estimated as barium sulphate and ammonium phosphomolybdate as in inorganic analysis. The phosphoric acid can be estimated also by precipitation as $\text{Mg}(\text{NH}_4)\text{PO}_4$, which is then ignited and weighed as $\text{Mg}_2\text{P}_2\text{O}_7$.

19. Micro-analysis. In certain bio-chemical processes, only minute quantities of valuable products are obtained, which are too small to be analysed by the ordinary methods of analysis. Hence in this branch of organic research simplified methods of "micro-analysis" have recently been devised, which have the further advantage of effecting a saving of gas and time. A few milligrammes of the substance to be analysed are weighed on a *micro-chemical balance* and combusted by means of CuO and PbCrO_4 in a current of oxygen. The combustion apparatus is of a special design and is much reduced in size. The resulting CO_2 and H_2O are absorbed in the usual manner. The nitrogen is estimated volumetrically by micro-Dumas' or micro-Kjeldahl's method.

QUESTIONS

1. Give with practical details the apparatus that you would use for determining the percentage composition of glucose. What modification in the apparatus would be necessary if you are required to estimate the percentage of carbon and hydrogen in (a) acetamide, and (b) acetyl chloride?

2. 0.2398 gm. of an organic substance, containing only C, H, and O, gave on combustion, 0.3506 gm. of CO_2 and 0.1446 gm. of H_2O . Calculate the percentage composition of the substance. (*Ans.* C=39.9% ; H=6.7% ; O=53.4%)

3. Describe how you would analyse an organic compound quantitatively for nitrogen (Dumas' method). Indicate the function of each of the important parts of the tube. (*Punjab, Inter., 1930*)

4. An organic compound gave the following results on analysis :—

0.1335 gm. gave 0.2948 gm. of CO_2 and 0.0603 gm. H_2O .

0.085 gm. gave 26.4 c.c. of dry nitrogen measured at 27° and 750 mm.

Calculate the percentage of C, H and N in the substance. What reason have you to believe that the substance contains no oxygen ?

(*Ans.* C=60% ; H=5% ; N=35%)

5. Describe Kjeldahl's method for the estimation of nitrogen in organic compounds. To what important classes of organic substances is the method applicable ?

6. An organic compound gave the following results on analysis :—

0.197 gm. gave 0.293 gm. CO_2 and 0.150 gm. H_2O .

By Kjeldahl's method 0.59 gm. required 10 c.c. of normal H_2SO_4 for the neutralization of ammonia.

(*Ans.* C=40.6% ; H=8.5% ; N=23.7% ; O=27.2%)

7. Describe in detail how you would proceed to estimate the percentage of nitrogen in a sample of cheese.

8. Explain Carius' method as applied in quantitative analysis of organic compounds. What elements may be estimated by this method ?

(*Punjab, Inter., 1920*)

9. Describe Dennstedt's method of analysis of organic compounds, and point out its advantages.

CHAPTER IV

DETERMINATION OF EMPIRICAL AND MOLECULAR FORMULÆ

20. Calculation of Empirical Formula. From the percentage composition of the substance, determined as given in the last chapter, the empirical formula, (which is the simplest expression of the ratio of the atoms of different elements present in the molecule), is calculated as follows :—

(1) The percentage of each element is divided by its atomic weight to get the relative number of atoms of the various elements present.

(2) The quotients thus obtained are then simplified by dividing them by the lowest value. The figures obtained either already are, or may be reduced to whole numbers, which express the simplest ratio of atoms of the various elements present.

Example 1. *The analysis of a substance containing carbon, hydrogen, and oxygen gave the following results :—*

C=68.84% ; H=4.92% ; and (by difference) O=26.24%. Calculate the empirical formula.

Dividing the percentage of each element by its atomic weight we get the atomic ratio,

$$C = \frac{68.84}{12} = 5.74$$

$$H = \frac{4.92}{1} = 4.92$$

$$O = \frac{26.24}{16} = 1.64.$$

Dividing by the smallest number, 1.64, we get the simplest atomic ratio : C=3.5, H=3, O=1. Hence the empirical formula of the substance is $C_7H_6O_2$.

21. Determination of Molecular Formula. To determine the molecular formula of a substance we must know : (1) the

empirical formula, and (2) the molecular weight. The molecular weight is divided by the empirical formula weight to get the nearest whole number. The empirical formula is then multiplied by this number to get the molecular formula.

To take a specific example, analysis shows the empirical formula of acetic acid to be CH_2O . Its molecular weight is found to be 60. We have

$$(30) \quad (\text{CH}_2\text{O})_n = 60; \text{ whence } n = 2.$$

The molecular formula of acetic acid is, therefore, $(\text{CH}_2\text{O})_2$ or $\text{C}_2\text{H}_4\text{O}_2$.

The molecular weights of organic compounds are almost invariably determined by physical methods given below. In a few cases chemical methods may also be helpful.

22. Molecular Weights of Volatile substances. From Avogadro's hypothesis it follows that equal volumes of different gases or vapours under similar conditions of temperature and pressure possess weights in the ratio of their molecular weights (since the number of molecules in each case is the same). Conversely a *gram-molecule* (*i.e.*, the molecular weight expressed in grams) of *any* gas or vapour must occupy the same volume under similar conditions of temperature and pressure. The volume occupied by a gram-molecule of a gas at N. T. P. is termed the *gram-molecular volume* (G. M. V.), and is found to be equal to 22.4 litres. This relation is made use of for the determination of molecular weights of gases and volatile substances. Another relation that is employed for the molecular weight determination of a substance in the gaseous state is the following :—

$$\text{Mol. Wt.} = \text{Vapour Density} \times 2.$$

23. Victor Meyer's Method. Of the various methods that are available for the determination of molecular weights of volatile substances (see a text-book of Physical Chemistry), Victor Meyer's method is the one almost universally employed in actual practice. A known weight of the substance is allowed to vaporize very rapidly. The vapour displaces its own volume of air which is collected over water and measured under the atmospheric conditions of temperature and pressure.

The apparatus employed is shown in Fig. 29. The inner tube, *A*, is thoroughly cleaned and dried, and an asbestos pad or a little sand is put at its bottom. It is then placed in the outer tube, *B*,

containing a liquid the boiling-point of which is at least 20° higher than that of the substance whose molecular weight is to be determined. The inner tube is corked, the end of the delivery-tube is immersed under water, and the liquid in the outer tube is boiled. When the temperature has become constant (*i.e.*, when no more air bubbles escape from the delivery tube), a graduated tube, *G*, filled with water is inverted over the end of the delivery-tube as shown in the figure. The cork is then momentarily removed and a weighed amount ($0.1-0.2$ gm.) of the substance contained in a tiny, stoppered bottle, is introduced. Since the temperature inside the tube is much higher than the boiling-point of the substance, the latter vaporizes rapidly and blows the stopper out of the tiny bottle. The vapour, rising up the tube, drives its own volume of the air into the measuring tube. The suddenness of vaporization and the shape of the tube are responsible for the displacement of air by the vapour of the substance.

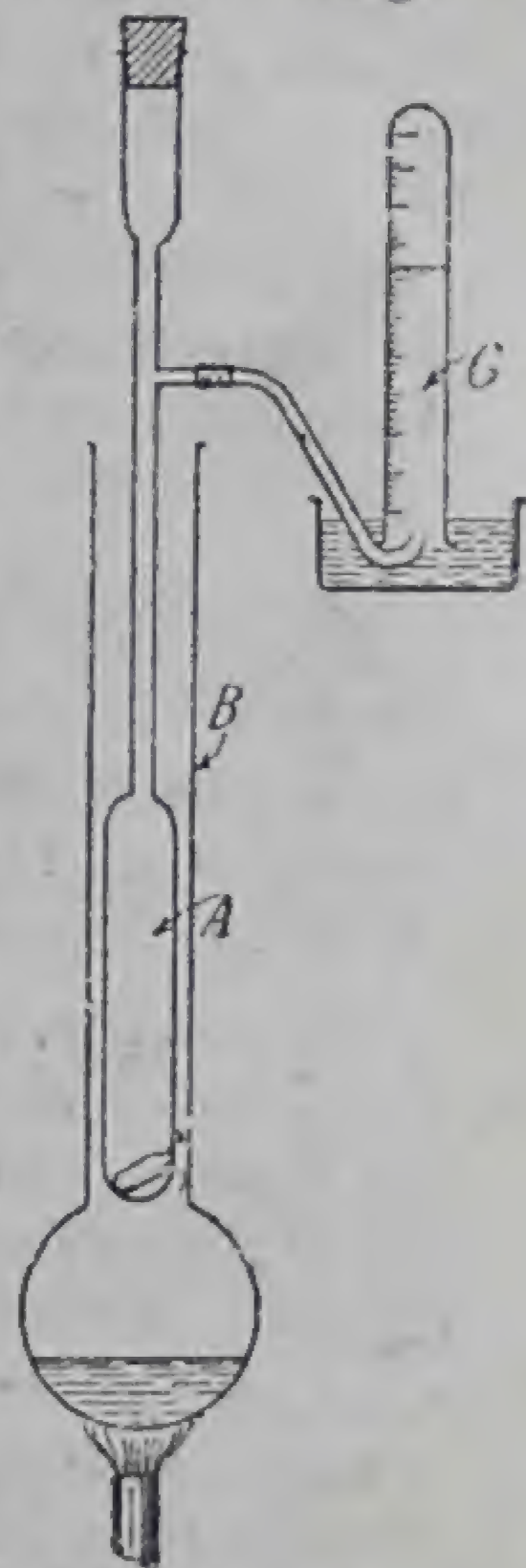


Fig. 29. Victor Meyer's Apparatus.

The measuring tube is now levelled in a hydrometer jar containing water, and the volume of the air noted. The temperature of the water in the trough and the barometric pressure are also recorded.

Example 2. *In a Victor Meyer apparatus, 0.146 gm. of chloroform displaced 30.5 c.c. of air, measured over water at 22°C , the barometric pressure being 755 mm. Calculate the molecular weight of chloroform. (Aqueous tension at $22^{\circ}\text{C}=20$ mm.)*

Barometric pressure = 755 mm.

Aqueous tension at $22^{\circ} = 20$ mm.

\therefore Pressure of dry air = 735 mm.

Volume of dry air reduced to N. T. P.

$$= 30.5 \times \frac{273 \times 735}{295 \times 760} \text{ c.c.} = 27.2 \text{ c.c.}$$

Hence, 0.146 gm. of chloroform, when in the state of vapour would occupy 27.2 c.c. at N. T. P. Therefore, the weight of the substance that would occupy 22.4 litres at N. T. P.

$$= 0.146 \times \frac{22.4 \times 1000}{27.2} \text{ gm.} = 120 \text{ gm.}$$

\therefore Molecular weight of chloroform = 120 .

24. Molecular Weights of Non-volatile Substances.

It is of course impossible to determine the molecular weight of a non-volatile substance (such as cane sugar) by Victor Meyer's method. In such a case the following two methods, based on the laws of osmotic pressure, are generally used. One of these methods involves the determination of the depression of the freezing-point, and the other the elevation of the boiling point of a pure solvent, caused by a given weight of a non-polar substance.

25. Freezing-point Method. *It can be shown (see a text-book of Physical Chemistry) that equimolecular quantities of different solutes dissolved in a given quantity of the same solvent produce the same depression of the freezing-point.*

The depression of the freezing-point produced by dissolving a gram-molecule of any non-electrolyte in 100 grams of a given solvent is termed the molecular depression of a solvent, and is denoted by K . Now, since the depression of the freezing-point is proportional to the quantity of the solute present, if we determine experimentally the depression, Δ , produced by s grams of the solute dissolved in 100 grams of the solvent, we can readily calculate the molecular weight, M , of the solute from the relation

$$\frac{M}{s} = \frac{K}{\Delta}$$

The following table gives the freezing-points of a few common solvents and the values of K , as determined experimentally :—

Solvent	Freezing-point	Molecular depression (K)
Water	0°	19
Acetic Acid	17°	39
Benzene	6°	52
Phenol	40°	75
Naphthalene	80°	69
Camphor	175°	400

The last three solvents are very useful since their melting-points are above the ordinary temperature and no cooling arrangement is, therefore, necessary. The high value of their depression constants and the non-hygroscopic nature of the last two are additional advantages. Camphor is specially noteworthy, since its molecular depression is so great as to make possible the use of an ordinary thermometer and a melting-point tube.

Beckmann's Apparatus. The Beckmann apparatus (Fig. 30) is the one chiefly used for the determination of molecular weights by the freezing-point method. It consists of the following parts:—

(i) A freezing-point tube, *A*, having a side-tube for introducing the solute and provided with a thermometer of a special design and a platinum stirrer, *P*. The thermometer has a scale comprising 6° and reading up to one-hundredth of a degree. The quantity of mercury in the bulb can be increased or decreased as desired by handling the small reservoir of mercury at the top of the scale. This makes it possible for the thermometer to be used for solvents having widely different freezing-points.

(ii) A wider tube, *B*, into which the freezing-point tube is fitted by means of a rubber ring. This provides an air-space round the freezing-point tube and keeps the latter from coming into direct contact with the freezing mixture.

(iii) A stout glass cylinder, filled with a suitable freezing mixture, in the cover of which is fixed the outer tube, *B*, as shown in the figure. A stirrer, *S*, also passes through the cover, and serves to stir up the freezing mixture.

From 15 to 20 grams of the solvent are placed in the tube, *A*, and weighed. The apparatus is set up as shown in the figure, and the glass cylinder is filled with a freezing-mixture at a temperature about 5° lower than the freezing-point of the solvent. *A* is removed from the air jacket and placed directly in the freezing mixture until the temperature of the solvent falls about half a degree below its freezing-point. The tube is then placed in the air-jacket and the liquid in it vigorously stirred. The crystals of the solvent begin to separate, and the temperature rises to a maximum which represents the freezing-point of the solvent. The operation is repeated to confirm the result obtained.

The tube, *A*, is now taken out of the air-jacket and a carefully weighed amount of the substance, the molecular weight of which is to be determined, is introduced through the side-tube. The liquid is stirred in order to dissolve the substance, and the tube is put back into the air-jacket. When the liquid has become slightly overcooled, it is stirred once again, and the *maximum* temperature reached is

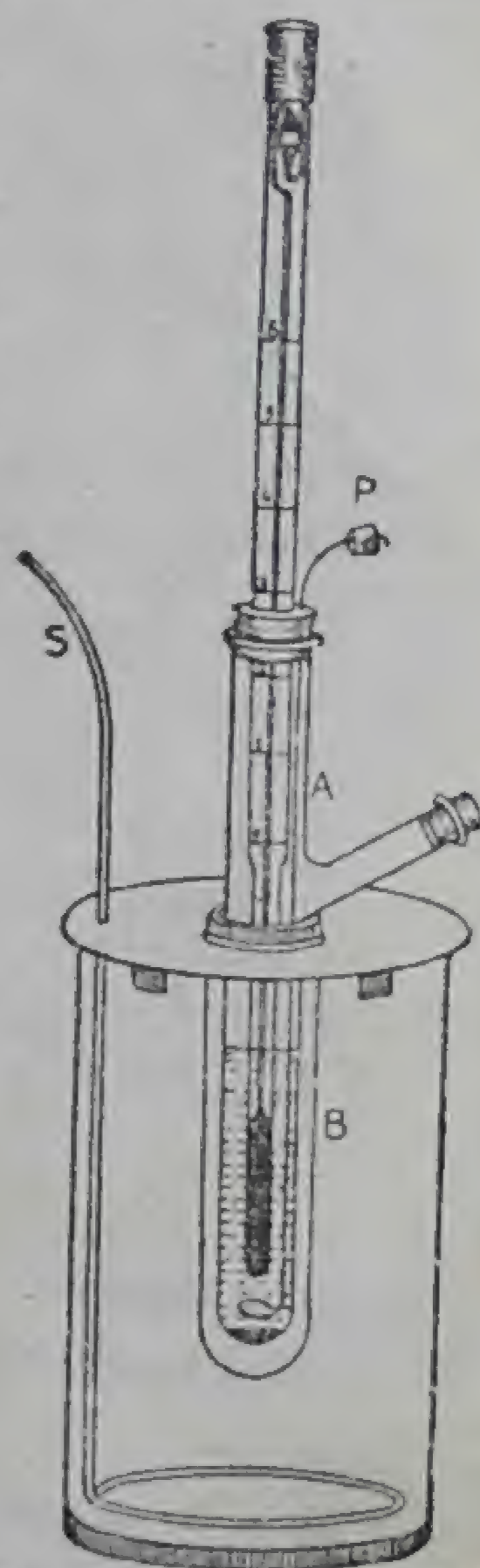


Fig. 30. Beckmann's Freezing-point Apparatus.

recorded. This gives the freezing-point of the solution. Another weighed quantity of the substance may be added to the same solution and the freezing-point determined.

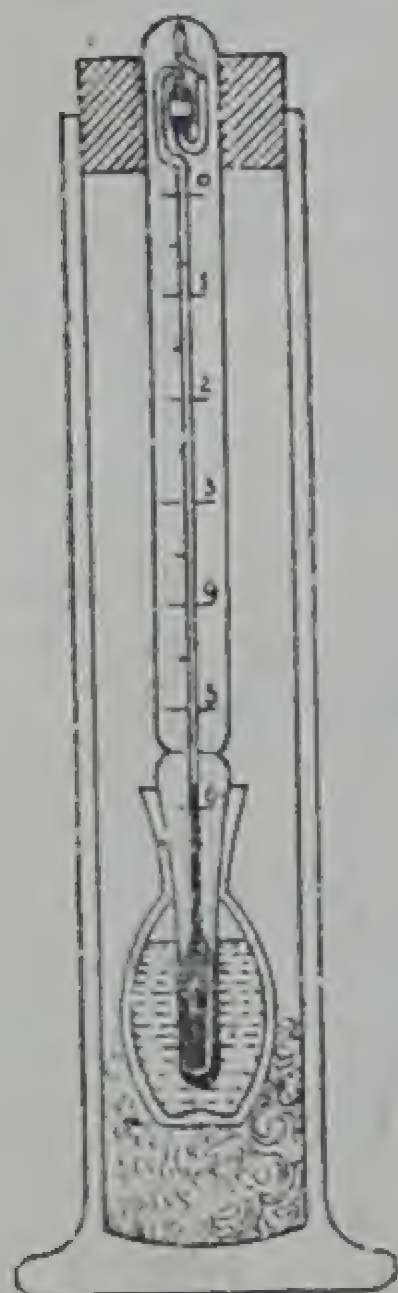


Fig. 31.
Eykman's
Depressimeter.

(2) **Eykman's Depressimeter.** For a rapid determination of the depression of the freezing-point, Eykman's apparatus (Fig. 31) is very convenient. It consists of a small flask, into the neck of which is ground a thermometer of the Beckmann type, but divided into twentieths of a degree. The combination is placed in a glass cylinder, where it is supported at the top by means of a cork and at the bottom by cotton wool. The latter, being a bad conductor of heat, retards cooling. Phenol is usually employed as the solvent. It is melted on a sand bath and poured into the flask so as to fill about three-quarters of it. The weight of the solvent is found by weighing the flask (along with the thermometer) before and after the introduction of phenol. The melting-point of the pure solvent (as indicated on the scale) is now determined by warming it until melted, and allowing it to cool in the glass cylinder with occasional shaking, until crystallization sets in. A weighed quantity of the substance under investigation is then introduced

and the freezing-point determined once again.

Example 3. *2.167 and 2.833 gm. of a substance were dissolved in 100 gm. of benzene. The depression of the freezing-point were 0.348°C and 0.452°C respectively. What was the molecular weight of the substance? The molecular lowering of freezing-point of benzene is 50°C .*

(Punjab, B.Sc. Hons., 1921)

If M is the molecular weight of the substance, we have

$$\frac{M}{s} = \frac{K}{\Delta}$$

where Δ is the depression of the freezing-point produced by s gm. of the substance dissolved in 100 gm. of the solvent. In the first experiment,

$$s = 2.167 \text{ gm.}$$

$$K = 50$$

$$\Delta = 0.348^{\circ}$$

Substituting these values in the above formula, we get :

$$M = \frac{50 \times 2.167}{0.348} = 311$$

Similarly, from the second experiment we have

$$M = \frac{50 \times 2.833}{0.452} = 313.$$

Hence, the mean value of the molecular weight from the experiments = 312.

26. Boiling-point Method. As in the case of the depression of freezing-point, it can be shown that *equimolecular quantities of different solutes dissolved in a given quantity of the same solvent produce the same elevation of the boiling-point.*

If M is the molecular weight of the substance, s the quantity of it in grams dissolved in 100 grams of the solvent, K the molecular elevation of the solvent (*i.e.*, the elevation of the boiling-point produced by dissolving a gram-molecule of any non-electrolyte in 100 gm. of the solvent), and Δ the observed elevation of the boiling-point, we have, as before :

$$\frac{M}{s} = \frac{K}{\Delta}$$

The following table gives the boiling points and molecular elevations of the solvents ordinarily used :—

<i>Solvent</i>	<i>Boiling-point</i>	K	K_1
Water	100°	5.2	5.4
Ethyl alcohol	78.0°	11.5	15.6
Ether	35.6°	21.1	30.3
Benzene	80.4°	26.0	32.0
Chloroform	61.0°	36.6	27.0
Acetone	56.3°	17.2	22.2

The constants in the last but one column, K , refer to 100 grams of the solvent; those in the last column K_1 , refer to 100 c.c. of the solvent at its own boiling point. These latter are used if we measure the *volume* of the solution instead of finding its weight.

Landsberger's Apparatus. The most convenient apparatus to use for the boiling-point determination is due to Landsberger (Fig. 32). It consists of the following parts :—

- (1) A boiling flask, F , in which the pure solvent is boiled.
- (2) A bulbed inner tube, B , which is graduated in c.c.'s. and has a hole, H , just above the bulb. It is provided with (i) a delicate thermometer, reading up to one-tenth of a degree, and (ii) a

delivery tube, *T*, which leads the vapour of the solvent from the boiling flask into the liquid placed in *B*. The lower end of this tube has a *rose* of small holes so as to effect a uniform distribution of the vapour through the liquid. The bulb serves to prevent portions of the liquid from being thrown out through *H* if the boiling becomes vigorous.

(3) An outer mantle, *M*, the lower end of which is connected to a condenser, *C*. The vapour from the boiling liquid in *B*, escaping through the hole *H*, forms a hot jacket round *B* and thus protects it from losing heat by radiation.

At first the boiling-point of the solvent is determined by placing 5 to 7 c.c. of it in *B* and passing the vapour of the boiling solvent from *F* into it. As soon as the temperature has become constant (which, as far as possible, should synchronize with the bulb of the thermometer being just completely covered by the liquid), the thermometer reading is taken. The boiling is now temporarily stopped, and the greater part of the liquid in *B* is poured back into *F*, only 5 to 7 c.c. being allowed to remain behind. A weighed amount of the substance whose molecular weight is to be determined is added to

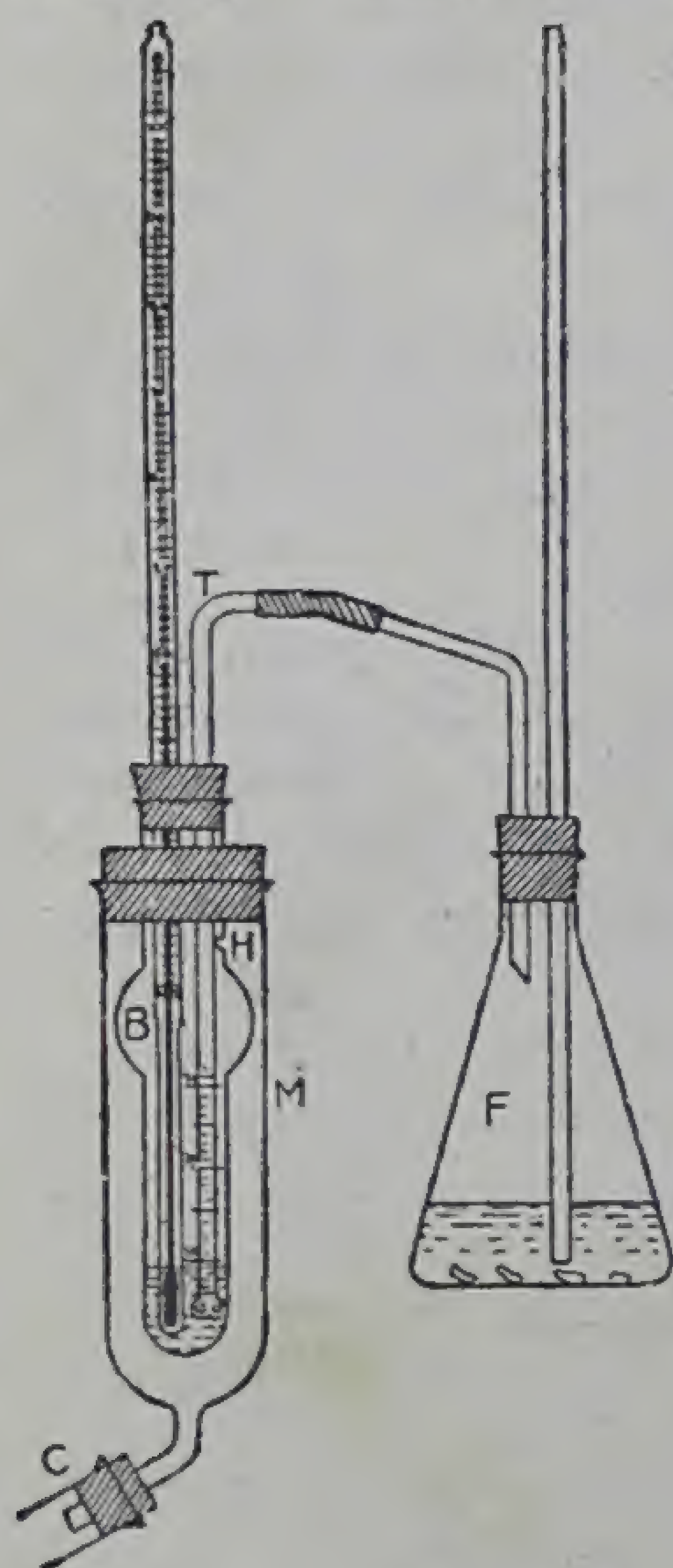


Fig. 32. Landsberger's Apparatus.

the solvent and the boiling-point determined as before. As soon as the temperature has been read off, the flask, *F*, is disconnected, so that more vapour might pass over. The thermometer and the delivery-tube are removed, and the volume of the liquid is read off, (or its weight determined). A second determination is made by passing in more of the vapour until the boiling-point is once again reached. The method of calculation is exactly similar to that given in the case of the freezing-point method.

Example 4. 0.562 gm. of a carefully purified substance when dissolved in 12.7 gm. of carbon disulphide ($K=23.7$) raised the boiling-point of the solvent by 0.784° . Calculate the molecular weight of the substance.

The quantity, *S*, of the substance present in 100 gm. of carbon disulphide

$$= \frac{0.562 \times 100}{12.7} \text{ gm.} = 4.42 \text{ gm.}$$

K for carbon disulphide = 23.7.

Elevation of the boiling-point, Δ , caused by 4.42 gm. of the substance dissolved in 100 gm. of carbon disulphide = 0.784°. If M is the molecular weight of the substance we have

$$\frac{M}{s} = \frac{K}{\Delta}$$

$$\therefore M = \frac{23.7 \times 4.42}{0.784} = 134.$$

27. Determination of Molecular Formula by Chemical Methods. Excepting the method given below for the determination of the molecular weight of a gaseous hydrocarbon, no purely chemical method is known by which the molecular weight of a substance can be established with certainty; all that we might do is to obtain information respecting the minimum value of the molecular weight or its reacting weight. The following are the important cases where chemical methods are helpful:—

(1) **Gaseous Hydrocarbons.** The molecular formula of a gaseous hydrocarbon can be determined as follows, no previous quantitative elementary analysis being necessary:—

(i) A known volume of the gas enclosed in an eudiometer tube is mixed with a known excess of oxygen, and the mixture exploded. Carbon and hydrogen of the hydrocarbon burn to produce carbon dioxide and water vapour. The residual gas is allowed to cool, in order to permit the condensation of water vapour, and then its volume is noted.

(ii) A strong solution of potassium hydroxide is now introduced into the eudiometer tube, which absorbs the carbon dioxide. When the absorption is complete, the volume of the gas (unused oxygen) is again noted.

From the volume of carbon dioxide produced from one volume of the hydrocarbon the number of carbon atoms in the molecule of the hydrocarbon is calculated with the help of Avogadro's hypothesis. The number of hydrogen atoms in the molecule is then found from the amount of oxygen used up in the production of water.

Example 5. 10 c.c. of a hydrocarbon and 45 c.c. of oxygen were enclosed in an eudiometer over mercury and exploded. After explosion and cooling, the volume of gases was reduced to 35 c.c. On addition of caustic soda, there was further reduction to 15 c.c. What is the composition of the hydrocarbon?

Volume of the hydrocarbon taken = 10 c.c.

“ “ CO₂ produced = 35 — 15 or 20 c.c.

“ “ O₂ used up = 45 — 15 or 30 c.c.

We see that 1 volume of the hydrocarbon gives on oxidation 2 volumes of CO_2 . Hence, by Avogadro's Hypothesis, 1 molecule of the hydrocarbon gives 2 molecules of CO_2 . It contains, therefore, two atoms of carbon.

One volume of the hydrocarbon is oxidized by 30/10 or 3 volumes of oxygen. Hence, by Avogadro's Hypothesis, one molecule of the hydrocarbon requires for complete oxidation 3 molecules of oxygen. Out of these, 2 molecules must have been used up for oxidizing the two atoms of carbon present in the molecule, and the remaining 1 molecule to burn the hydrogen to water. Now, one molecule of oxygen can oxidize two molecules of hydrogen to water,



Hence, a molecule of the hydrocarbon contains four atoms of hydrogen.

\therefore Formula of the hydrocarbon is C_2H_4 .

(2) Organic Acids. There exists the following relation between the molecular weight of an acid, its equivalent weight and basicity :

$$\text{Mol. Wt.} = \text{Eq. Wt.} \times \text{Basicity}$$

Hence the determination of the molecular weight of an acid involves the determination of (i) its basicity, and (ii) its equivalent weight. The basicity of an organic acid may be found by a study of its salts and esters. Thus, acetic acid gives rise to only one series of salts and esters. It must, therefore, in all probability, be a monobasic acid. Tartaric acid forms two potassium salts, a normal potassium tartrate and an acid potassium salt. It appears, therefore to be dibasic.

The equivalent weight of an organic acid, may be determined either volumetrically or gravimetrically. In the volumetric method a suitable known weight of the acid is titrated against standard barium hydroxide, using phenolphthalein as the indicator. The result is calculated as in Example 7 given below.

The gravimetric method for the determination of the equivalent weight of an acid involves the preparation of a pure sample of its silver, calcium or barium salt. The salt is then analysed to find the amount of the metal contained in a given weight of it. Silver salts are preferred for the equivalent weight determination, as they can be readily obtained pure and anhydrous, and are easily decomposed by heat to metallic silver. A suitable quantity of the acid is dissolved in a slight excess of dilute ammonia. The excess of ammonia is then boiled off and to the neutral solution thus obtained is added a slight excess of silver nitrate. The precipitate of silver salt is washed and dried. A known weight of the salt is then carefully heated in a crucible so as to decompose it until a constant weight is obtained. From the weight of silver salt taken and that of silver left behind

the equivalent weight of the acid is calculated as in Example 6 given below.

Example 6. On combustion 0.20 gram of a dibasic organic acid gave 0.040 gram of water and 0.195 gram of carbon dioxide. It contained no nitrogen. When 0.50 gram of its silver salt was ignited, it gave a residue of 0.355 gram of metallic silver. Find the empirical and molecular formula of the acid.

The empirical formula of the acid calculated as in Example 1 comes to CHO_2 .

The equivalent weight of the silver salt

$$= \frac{0.500}{0.355} \times 108 \text{ or } 152.$$

Hence the equivalent weight of the acid

$$= 152 - 108 + 1 \\ = 45.$$

And, since the acid is dibasic, the molecular weight is 90, which is twice the empirical formula weight. Hence the molecular formula of the acid is $\text{C}_2\text{H}_2\text{O}_4$.

Example 7. An organic monobasic acid gave the following combustion data :—

0.100 gm. gave 0.2525 gm. of CO_2 and 0.0432 gm. of H_2O . 0.122 gm. of the acid required 10 c.c. N/10 barium hydroxide solution for neutralization. What is the formula of the acid? (Punjab, Inter., 1931)

The percentage composition of the given acid is :—

$$\text{C} = 0.2525 \times \frac{12}{44} \times \frac{100}{0.100} \text{ or } 68.9$$

$$\text{H} = 0.0432 \times \frac{2}{18} \times \frac{100}{0.100} \text{ or } 4.8$$

$$\text{O} = 100 - (68.9 + 4.8) = 26.3.$$

Dividing the percentage of each element by its atomic weight, we get the atomic ratio :—

$$\text{C} = \frac{68.9}{12} \text{ or } 5.74 ; \quad \text{H} = \frac{4.8}{1} \text{ or } 4.8 ; \quad \text{O} = \frac{26.3}{16} \text{ or } 1.65 ;$$

Dividing by the smallest figure, 1.65, we get the simplest atomic ratio :—

$$\text{C} = 3.48, \quad \text{H} = 2.91, \quad \text{O} = 1.$$

Hence, the empirical formula of the acid is $\text{C}_7\text{H}_6\text{O}_2$.

Empirical formula weight = $84 + 6 + 32$ or 122.

Now, quantity of the acid neutralized by 10 c.c. of N/10 $\text{Ba}(\text{OH})_2$ = 0.122 gm.

\therefore Quantity of the acid neutralized by a litre of normal $\text{Ba}(\text{OH})_2$ solution, i.e., the equivalent weight of the acid

$$= 0.122 \times 100 \times 10 \text{ or } 122.$$

Since the acid is monobasic, its molecular weight is 122, which, as we have seen above, is also its empirical formula weight. Hence the molecular formula must be $C_7H_6O_2$.

As the acid is monobasic, and contains therefore only one carboxyl group, its constitutional formula must be $C_6H_5.COOH$.

(3) Organic Bases. Most organic bases combine with hydrochloroplatinic acid, H_2PtCl_6 , giving sparingly soluble platinichlorides. The general formulæ of the platinichlorides derived from mono- and di-acid bases are respectively $B'H_2PtCl_6$ and $B''H_2PtCl_6$ where B' and B'' represent one molecule of the mono-acid and of the di-acid base. On being caustiously heated, the platinichlorides decompose, leaving a residue of metallic platinum. Since the atomic weight of platinum is 195, the weight of the platinichloride that yields this amount of the metal represents its molecular weight. If the acidity of the base is known its molecular weight can be calculated as in the following example.

Example 8. *A mono-acid organic base gave the following results on analysis :—*

0.100 gm. gave 0.288 gm. CO_2 and 0.0756 gm. water.

0.200 gm. gave 21.8 c.c. of nitrogen at $15^\circ C$ and 760 mm.

0.400 gm. of the platinichloride left, on ignition, 0.125 gm. of platinum.

What is the molecular formula of the base ? (Pt.=195)

(Punjab, B.Sc., 1935)

The empirical formula of the base calculated as in the previous examples comes to C_7H_9N .

If B is the molecular formula of the base, the formula of the platinichloride should be $B_2H_2PtCl_6$. A gram molecule of the platinichloride would leave on ignition 195 grams of pure platinum. Hence, the molecular weight of the platinichloride, $B_2H_2PtCl_6$

$$= 0.400 \times \frac{195}{0.125} \text{ or } 624.$$

\therefore the Molecular Weight of the base B

$$= \frac{624 - (2 + 195 + 213)}{2} = 107.$$

This is identical with the empirical formula weight. Hence, the molecular formula of the base is the same as its empirical formula, i.e., C_7H_9N .

(4) Other Compounds. Most organic substances are neither acids nor bases. In the case of such substances it is often impossible to determine the molecular weight by purely chemical methods. A detailed study of the chemical behaviour of the substance may sometimes lead to a definite conclusion. Thus, benzene (empirical formula, CH) yields a derivative having the empirical formula C_6H_5Br . Hence

it follows that the benzene molecule must contain 6 (or a multiple of 6) carbon atoms, and the molecular formula must be C_6H_6 (or $C_{12}H_{12}$, $C_{18}H_{18}$, etc.) A multiple of 6 is, however, out of the question, since no derivative, has ever been obtained from benzene which indicates the possibility of replacing, *e.g.*, $\frac{1}{12}$ or $\frac{1}{18}$ of the total hydrogen. Hence the formula of benzene must be C_6H_6 .

28. Law of Even Numbers. The general formula of saturated hydrocarbons is C_nH_{2n+2} . Hence, the molecule contains an even number of hydrogen atoms. Now, all the other organic compounds can be regarded as derived from the saturated hydrocarbons by the replacement of these hydrogen atoms by other atoms or groups, or by the removal of an even number of hydrogen atoms, or by both these causes. Hence the sum of the valencies of all the atoms present in the molecule of a compound must always be an even number. Thus the molecular formula of a substance having the empirical formula C_3H_2Br must at least be twice this, since the sum of the valencies of all the atoms ($4 \times 3 + 2 + 1 = 15$) is an odd number.

QUESTIONS

1. How is the empirical formula of a substance calculated from the results of quantitative elementary analysis?

2. An organic compound gave the following results on analysis:

0.2033 gm. gave on combustion 0.3780 gm. CO_2 and 0.1288 gm. water.

0.1877 gm. of the compound gave on combustion 31.7 c.c. of moist nitrogen measured at $14^\circ C$ and 758 mm. pressure. What is the empirical formula of the compound? (Aqueous tension at $14^\circ C = 12$ mm.) (Punjab, Inter., 1925)

3. What do you understand by the molecular formula of a substance, and what are the data necessary for its determination?

4. State the principle on which the determination of molecular weights of volatile substance is based. Describe in detail the Victor Meyer method for the determination of molecular weights.

5. 0.37 gm. of a substance, containing carbon, hydrogen, and oxygen, gave on combustion 0.66 gm. of CO_2 and 0.27 gm. of water. Further, 0.123 gm. of the substance displaced 39.6 c.c. of air at $17^\circ C$ and 760 mm. in Victor Meyer's apparatus. Ascertain from these data the molecular formula of the substance. (Inter., B.Sc., Manc., 1906)

6. In a determination of the molecular weight of a substance by Victor Meyer's method, 0.1680 gm. of the substance gave 49.4 c.c. of vapour at $20^\circ C$ and 740 mm. pressure. Calculate the molecular weight of the substance. (Punjab, B.Sc., Agr., 1926)

7. Describe how you would proceed to determine the molecular weight of a non-volatile, solid organic compound.

8. On what principle is the freezing-point method of molecular weight determination based? Describe carefully the apparatus used and the method of procedure.

9. 3.29 gm. of a substance dissolved in 100 gm. of water ($K=19$) gave a depression of the freezing-point of $2.04^\circ C$. Determine the molecular weight of the substance. (London, Inter., 1908)

10. Describe Landsberger's apparatus for the determination of elevation of the boiling-point, and explain its working.

11. 0.6 gram of a substance was dissolved in 10 grams of acetone. An elevation of $1.67^\circ C$ was observed in the boiling-point of the solvent. Calculate the molecular weight of the solvent. (Punjab, B.Sc., 1914)

K for acetone is 16.7.

12. In what cases of organic compounds may purely chemical methods of molecular weight determination be used? Describe the method employed in each case.

13. Describe briefly how you would proceed to determine the molecular formula of a gaseous hydrocarbon. (Punjab, Inter., 1919)

14. 12 c.c. of a gaseous hydrocarbon were mixed with 90 c.c. of oxygen, and the mixture exploded. After explosion, the volume was 72 c.c. On adding KOH, 36 c.c. of the gas disappeared, leaving oxygen only. What is the molecular formula of the gas? All the above measurements were made at 15°C and 755 m.m. pressure, the gases being saturated with moisture. (Aq. tension, at $15^{\circ}\text{C} = 12.7$ mm.) (Punjab, Inter., 1919)

15. An organic tribasic acid gave the following results on analysis :

0.1584 gm. gave 0.2368 gm. CO_2 and 0.0655 gm. H_2O .

0.2219 gm. of the normal silver salt, on being carefully ignited, gave 0.1458 gm. of pure silver.

What is the molecular formula of the acid?

16. An organic monobasic acid gave the following combustion data :—

0.100 gm. gave 0.2525 gm. of CO_2 and 0.0432 gm. of H_2O .

0.122 gm. of the acid required 10 c.c. of N/10 caustic soda solution for neutralization.

What is the molecular formula of the acid?

(Punjab, Inter., 1931)

17. A mono-acid organic base gave the following results on analysis :—

0.100 gm. gave 0.2882 gm. CO_2 and 0.0756 gm. water.

0.200 gm. gave 21.8 c.c. of nitrogen at 15°C and 760 mm.

0.400 gm. of the platinichloride left, on ignition, 0.125 gm. of platinum.

What is the molecular formula of the base? (Pt = 195; Aqueous tension at $15^{\circ}\text{C} = 13$ mm.) (Punjab, BSc., 1935)

18. Explain the Law of the Even Numbers and its utility in the determination of the molecular formula of an organic compound.

ANSWERS

2. $\text{C}_3\text{H}_2\text{NO}$.

9. 31.

15. $\text{C}_6\text{H}_8\text{O}_6$.

5. $\text{C}_3\text{H}_6\text{O}_2$.

11. 60.

16. $\text{C}_7\text{H}_6\text{O}_2$.

6. 83.

14. C_3H_6 .

17. $\text{C}_7\text{H}_9\text{N}$.

CHAPTER V

MOLECULAR STRUCTURE AND ISOMERISM

29. Isomerism. Among inorganic compounds the empirical formula is in almost all cases sufficient to characterize the substance in hand. Thus there is but one substance having the formula CuSO_4 , only one having the formula HCl , and so on. In organic compounds, on the other hand, even the molecular formula is not sufficiently characteristic to eliminate the possibility of confusion with other compounds. There may be many organic compounds having exactly the same molecular formula, which nevertheless differ from one another in their physical and chemical properties. Such compounds are called *isomers* or *isomerides*, the phenomenon being termed *isomerism*.

There are, for example, two different compounds having the molecular formula $\text{C}_2\text{H}_6\text{O}$, five having the formula $\text{C}_3\text{H}_8\text{O}$, and as many as eighteen having the formula C_8H_{18} . The number of isomers theoretically possible in the case of compounds having higher molecular weight may be very large indeed. Thus there are 75 possible isomers for the molecular formula $\text{C}_{10}\text{H}_{22}$, 159 for $\text{C}_{11}\text{H}_{24}$, and 802, for $\text{C}_{13}\text{H}_{28}$. All the isomers theoretically possible in a given case, are, however, not necessarily known.

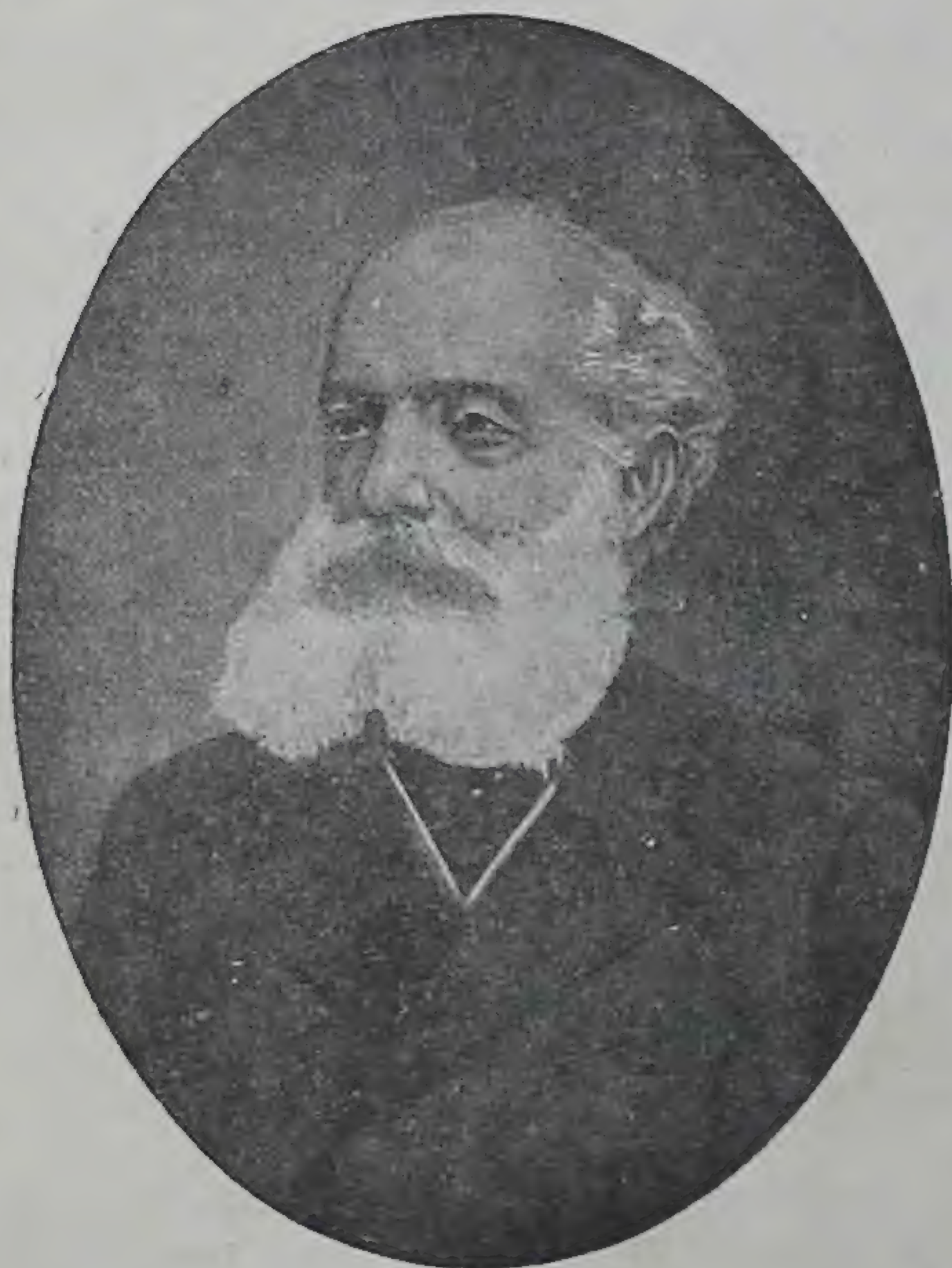
The difference in physical and chemical properties of isomeric substances is to be sought in the internal structure of the molecules, the atoms in which are, in each case, assumed to be differently arranged. This difference of arrangement may be due—

(1) To the way in which the atoms are linked with one another, without reference to their relative position in space. These are cases of *structural isomerism*, which we shall discuss presently.

(2) To the relative position of the atoms in space. These are cases of *stereoisomerism*, and will be discussed later (See Chapter VIII).

30. Molecular Structure (*Kekulé and Couper's Theory*). In 1858, Kekulé published his famous paper "*On the Constitution and Metamorphoses of Chemical Compounds and on the Chemical Nature of Carbon*." In this he advanced two hypotheses upon which the modern structural formulæ are based. The first of these postulated that *carbon is a tetravalent element* and the second that *its atoms have the capacity to link with one another*. Shortly after the appearance of

Kekulé's publication Couper expressed similar views in a paper published in a French scientific journal.

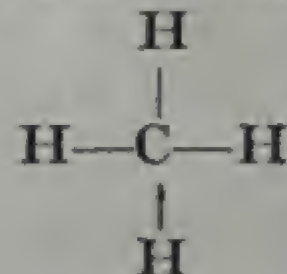
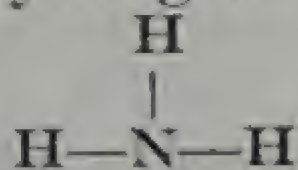
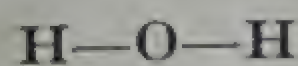


FRIEDRICH AUGUSTE
KEKULE (1829—1896)

Kekulé was born at Darmstadt, Germany. He studied chemistry at Giessen and Paris. In 1856, he became a *privat-docent* at the University of Heidelberg. There in 1858 he published his memorable paper "*On the Constitution and Metamorphoses of Chemical Compounds and on the Chemical Nature of Carbons.*" The immediate result of this famous publication was that he was called to the chair of Chemistry in the University of Ghent. Here he published his classical *Lehrbuch der Organischen Chemie* and in 1865 developed the famous *Benzene Theory*.

In 1867, Kekulé was called to Bonn to take charge of the newly-erected laboratory designed by Hofmann. There he continued to teach until his death in 1896.

By the aid of the above two hypotheses we can represent graphically the molecular architecture of the majority of organic compounds. The combining capacity or *valency* of an atom is indicated by joining the symbols of the elements concerned in the union by small lines or dots, so that each line or dot represents a unit of valency. It is assumed that in the formation of a compound the valencies of the atoms undergoing combination are mutually used up. Hence the elements which, like hydrogen, are monovalent must combine according to the formula $H-X$. Similarly di-, tri-, and tetravalent elements must combine with hydrogen as in the following:—

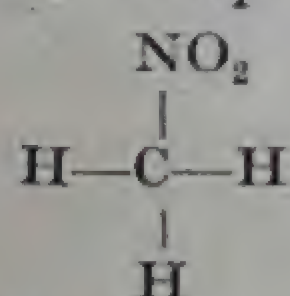
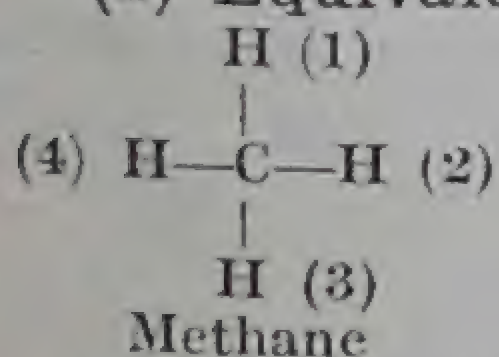


While in inorganic compounds elements do not always show the same valency, among organic compounds variable valency is rather the exception than the rule. The elements, carbon, hydrogen and oxygen, of which the majority of organic compounds are composed, show, in almost all cases, a valency of four, one and two respectively.

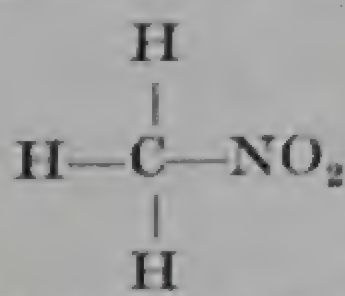
The way in which the various atoms in a molecule are linked together indicates the structure or constitution of the compound. It is expressed by structural or constitutional formulae. In writing the structural formulae the following rules, based on experience, are observed :—

(1) **Tetravalency of Carbon.** The carbon atom is usually tetravalent, and may thus combine with at the most four univalent atoms or groups. Thus in methane and carbon tetra-chloride one atom of carbon is combined with four atoms of hydrogen and chlorine respectively.

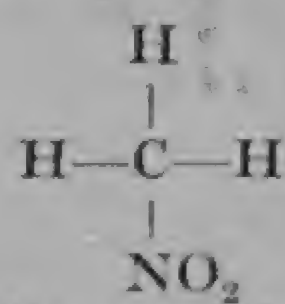
(2) **Equivalence of the Four Valencies.** The four valencies of a carbon atom are equivalent to one another since the replacement of *any* one of the four hydrogen atoms of the methane molecule by a monovalent substituent always gives the same product. A formal proof of this has been furnished by Henry, who prepared nitromethane in four different ways, so that each time the nitro group replaced a *different* hydrogen atom. If we designate the four hydrogen atoms as 1, 2, 3, and 4, as in the margin, we may formulate the four possible compounds as follows :—



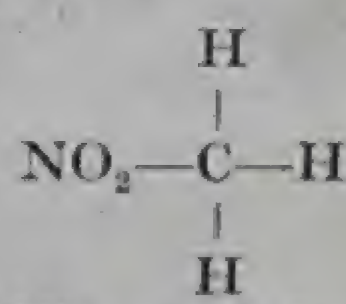
1-Nitro-Methane



2-Nitro-methane



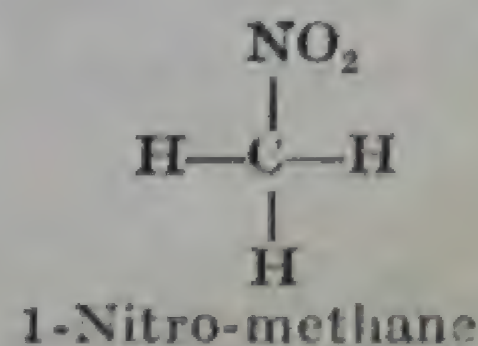
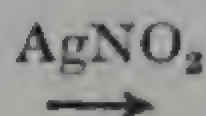
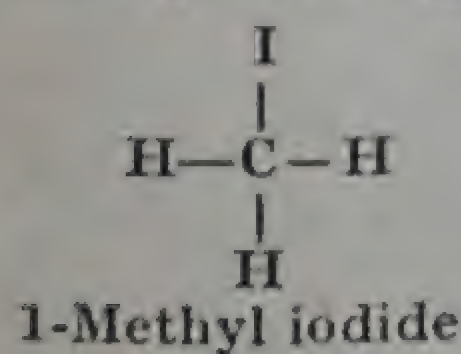
3-Nitro-methane



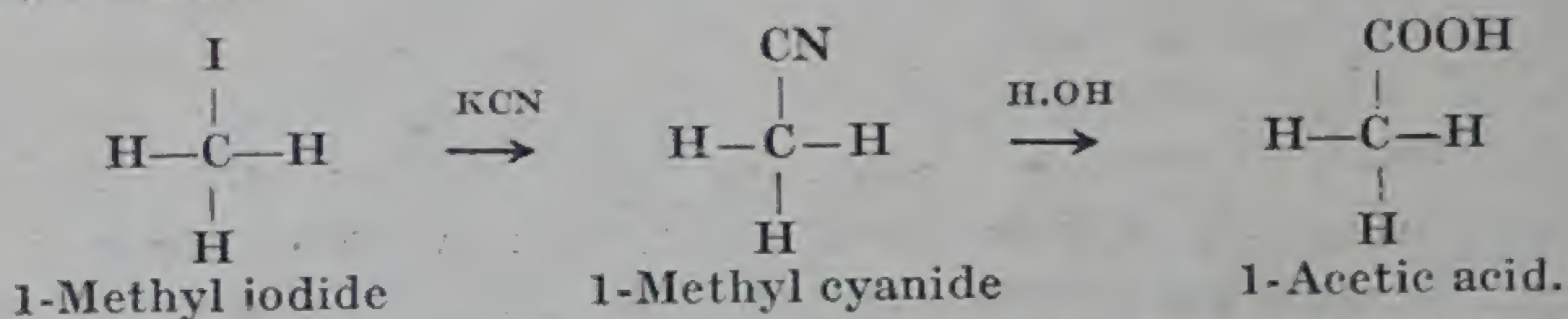
4-Nitro-methane

All of these were prepared as given below, and were shown to be identical :—

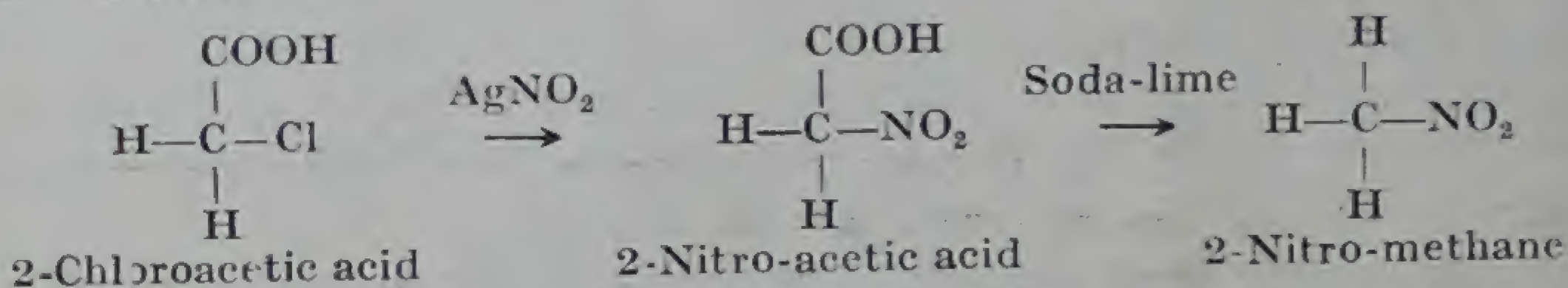
(i) Henry started with methyl iodide, in which we may assume that iodine occupies the position 1. It was directly converted into 1-nitro-methane by heating with silver nitrite :—



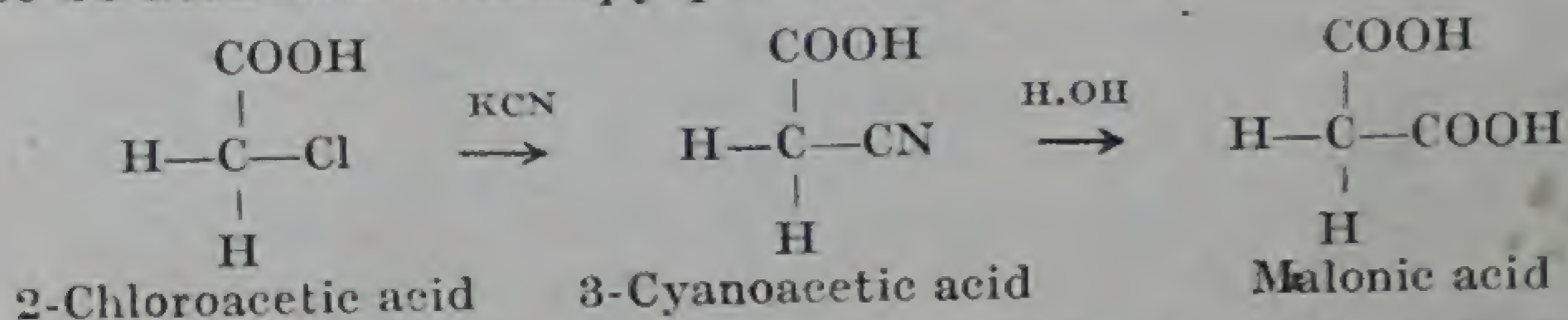
(ii) Another portion of methyl iodide was converted into acetic acid as shown below :—



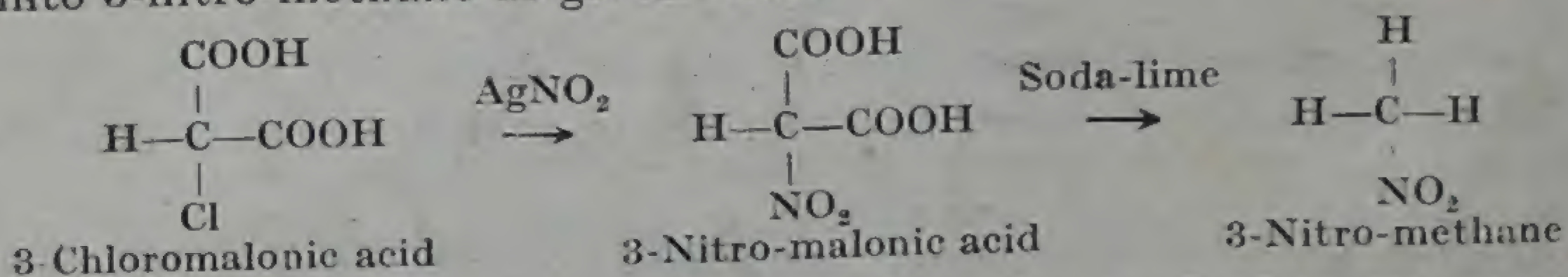
This on chlorination gave chloroacetic acid, in which the chlorine atom must necessarily possess a position other than 1, which we may assume to be 2. The chloroacetic acid was converted into 2-nitro-methane as given below :—



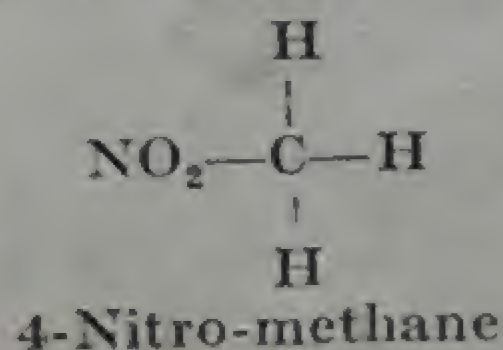
(iii) The chloroacetic acid, prepared as above, was then converted, as given below, into malonic acid in which the two carboxyl groups must be assumed to occupy positions 1 and 2 :



Malonic acid, on chlorination, gave mono-chloromalonic acid, in which the chlorine atom must occupy a position other than 1 and 2, which may be assumed to be 3. The chloromalonic acid was converted into 3-nitro-methane as given below :—

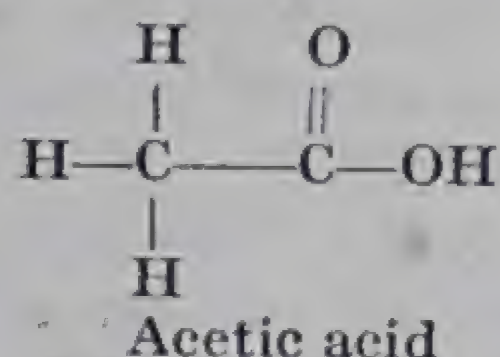
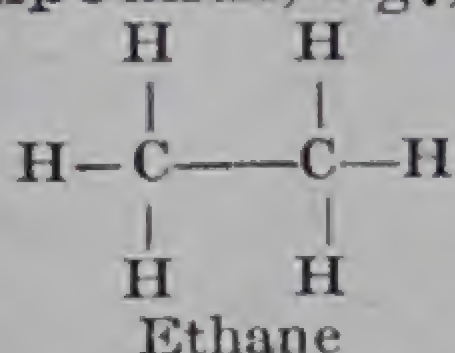


(iv) Starting with chloromalonic acid and introducing yet another carboxyl group, followed by chlorination, treatment with KCN, and soda lime, the fourth nitromethane was obtained :—

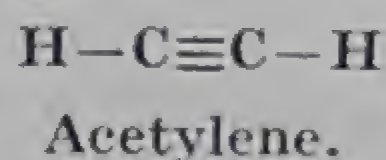
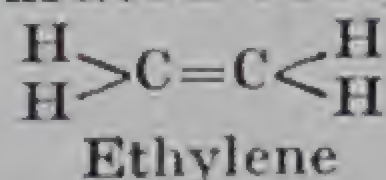


As already stated, the four nitromethanes obtained as above were found to be identical, thus proving the equivalence of the four valencies of a carbon atom.

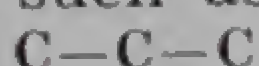
(3) **Linking of Carbon Atoms.** Carbon atoms possess a great capacity to link with one another. In the formation of carbon links it is assumed that each carbon atom is bound by 1, 2, or 3 valencies to a neighbouring carbon atom, and the remaining valencies can then be saturated by hydrogen, oxygen, chlorine, etc. Those compounds in which only singly bound carbon atoms are present are termed **saturated compounds**, *e.g.*,



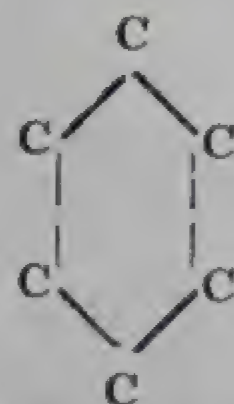
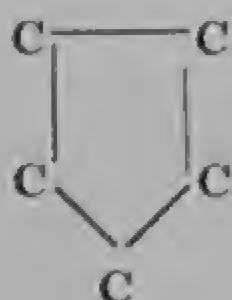
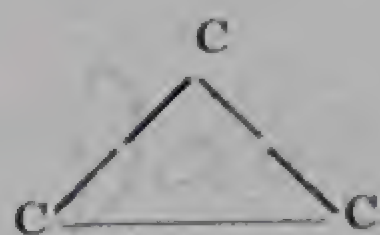
while those containing carbon atoms linked by double or triple bonds are called **unsaturated compounds**, *e.g.*,



Similarly, three or more carbon atoms may link together forming an open chain such as

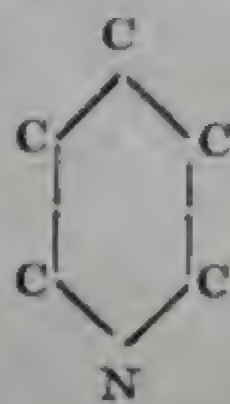
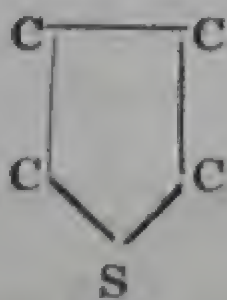
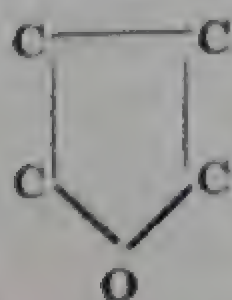


or a closed chain or ring such as



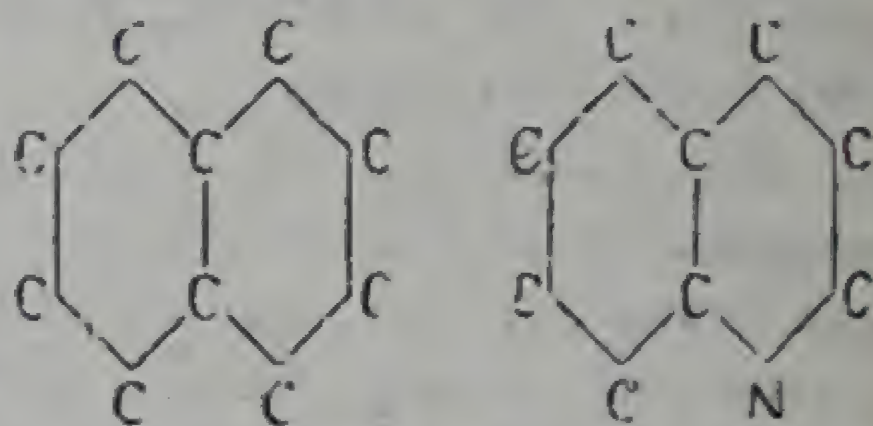
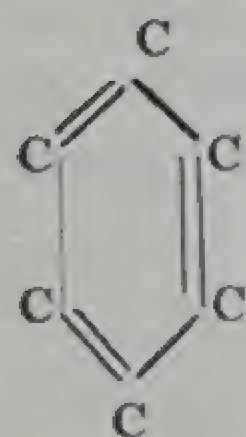
Some important open-chain compounds, are present in fats and oils. For this reason, the branch of organic chemistry that deals with open-chain compounds is called the **fatty or aliphatic series**, and a substance belonging to this class is known as a *fatty or aliphatic compound*.

Substances containing closed chains are termed **cyclic compounds**. If the rings are composed entirely of carbon atoms, they are called **carbocyclic**; if they contain, in addition to carbon, one or more atoms of some other polyvalent element, as in the following cases,



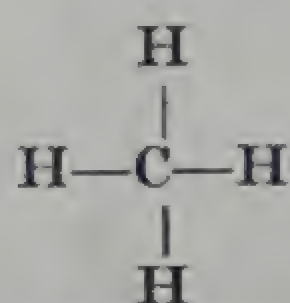
they are termed **heterocyclic**.

In addition to substances containing simple carbocyclic and heterocyclic rings of the above types, compounds containing two or more condensed rings, such as those shown in the margin, are known. In these compounds each pair of rings possesses two carbon atoms in common.

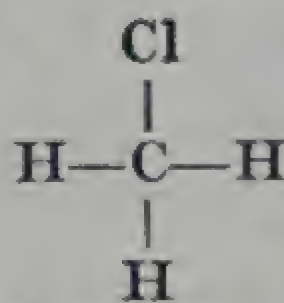


Among carbocyclic compounds those containing rings of six carbon atoms with alternate single and double bonds, as shown in the left-hand margin, are of great importance, and are called aromatic compounds or benzene derivatives.

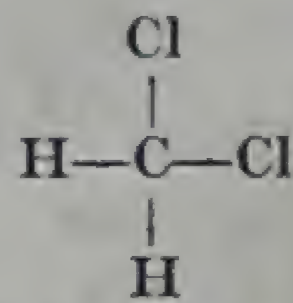
31. Substitution. The atoms of an element present in the molecule of an organic substance may be replaced or *substituted* by an equivalent number of atoms of other elements. Thus the four hydrogen atoms of methane can be successively replaced by atoms of chlorine.



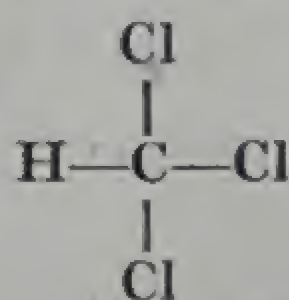
Methane



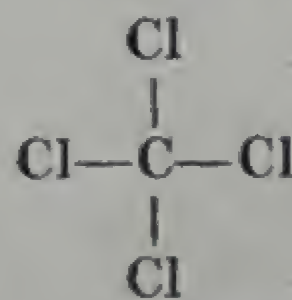
Monochloro-methane



Dichloro-methane

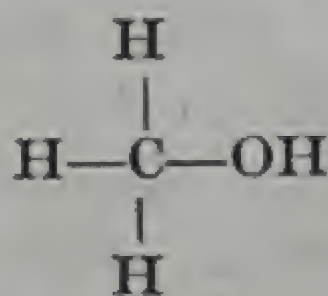
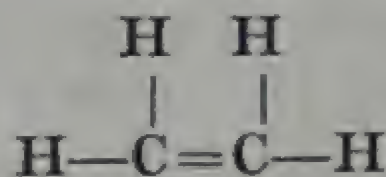


Trichloro-methane



Tetrachloro-methane

They may also be replaced by mono-, di-, or trivalent groups. Thus we get :

Methyl¹ alcoholMethylene¹ methane
or EthyleneMethenyl methane
or Acetylene.

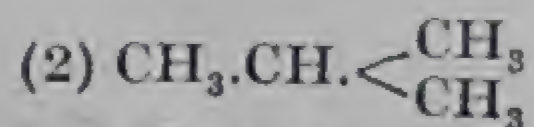
32. Nuclear Isomerism (Chain Isomerism). If an atom of hydrogen in the methane molecule be replaced by a methyl group, the hydrocarbon ethane, $\text{CH}_3.\text{CH}_3$; is obtained. Similarly, if one of the

¹ The mono-, di- and trivalent methane residues, $-\text{CH}_3$, $>\text{CH}_2$ and >CH are known respectively as *methyl*, *methylene* and *methenyl* groups.

hydrogen atoms of ethane be replaced by methyl group, we get propane, $\text{CH}_3.\text{CH}_2.\text{CH}_3$. Since all the hydrogen atoms of methane and also those of ethane are in a similar state of combination, there is only one ethane or propane possible. This is, however, not the case with propane, which contains hydrogen in two *different* states of combination. Hence the replacement of hydrogen by the methyl group gives in this case two different hydrocarbons :



Normal butane

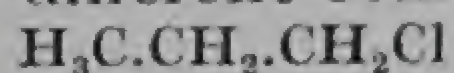


Isobutane

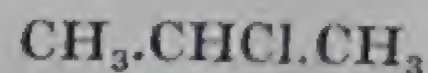
having the same composition, C_4H_{10} .

The cause of isomerism in butanes, as in numerous other compounds, is the difference in the constitution of the carbon chains. Normal butane has a *straight* chain of carbon atoms while isobutane has a *branched* chain. Isomerism of this type, involving a difference in structure of the carbon chain or nucleus, is called "chain" or "nuclear isomerism."

33. Position Isomerism. If a hydrogen atom of propane be replaced by an atom of chlorine or some other monovalent element, we get two different compounds :—



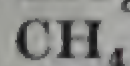
1-Chloropropane or Normal propyl chloride



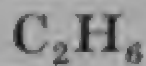
2-Chloropropane or Isopropyl chloride

The difference between these compounds lies not in the carbon chain itself but in the different *positions* of the substituent in the same carbon chain. Isomerism of this type is termed "position isomerism."

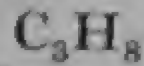
34. Homologous Series. On comparing the formulæ of hydrocarbons derived from methane by the successive replacement of hydrogen by methyl groups, as described above, we find that each successive member of the series has one atom of carbon and two of hydrogen more than its predecessor :—



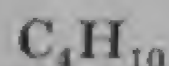
Methane



Ethane



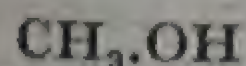
Propane



Butane

If the number of carbon atoms in the molecule of any of the above hydrocarbons be expressed by n , the number of hydrogen atoms will be found to be $2n+2$. This is true for the higher members as well. The series, therefore, possesses the general formula $\text{C}_n\text{H}_{2n+2}$.

Now if we replace a 'hydrogen' atom in the above hydrocarbons by a hydroxyl group, we obtain the following series :



Methyl alcohol



Ethyl alcohol



Propyl alcohol



Butyl alcohol

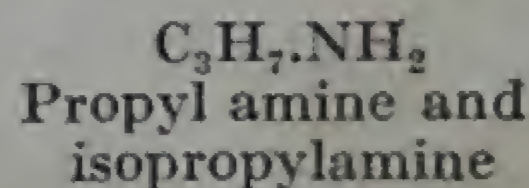
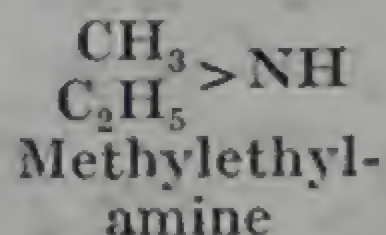
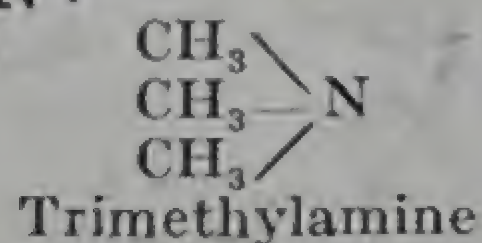
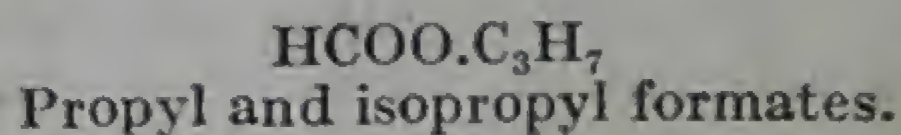
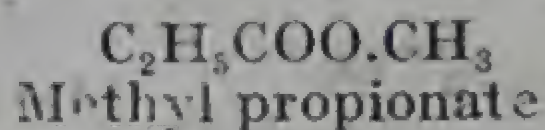
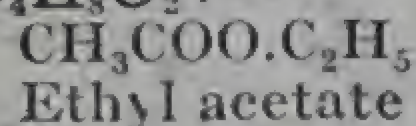
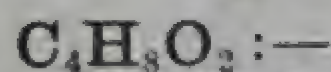
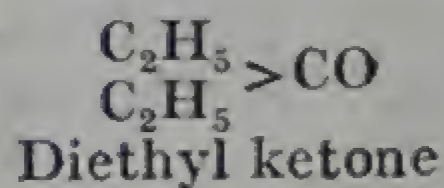
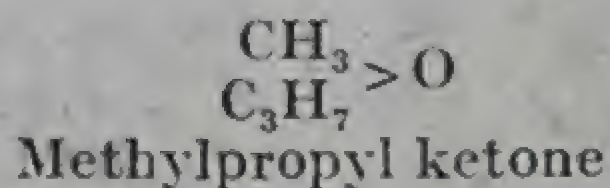
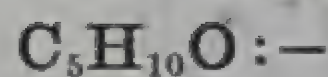
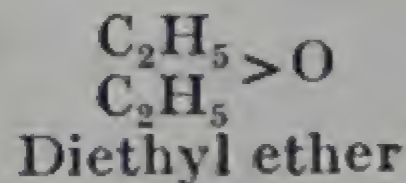
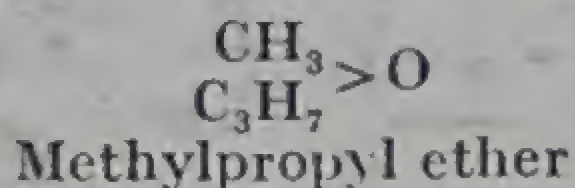
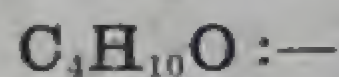
Here also we find that each member of the series differs from the preceding one by CH_2 , and the whole series may be expressed by the general formula $\text{C}_n\text{H}_{2n-1}\cdot\text{OH}$.

Replacement of the hydrogen of hydrocarbons by other groups or atoms always results in the formation of various series of compounds, whose successive members differ by CH_2 , and which may be represented by general formulæ as in the above two cases.

A group of similarly constituted compounds, any two consecutive members of which differ in molecular composition by CH_2 , is termed a homologous series, and its various members are known as homologues.

The various members of a homologous series possess, owing to similar molecular constitution, similar chemical properties; and their physical properties have been found to undergo a gradual change from member to member.

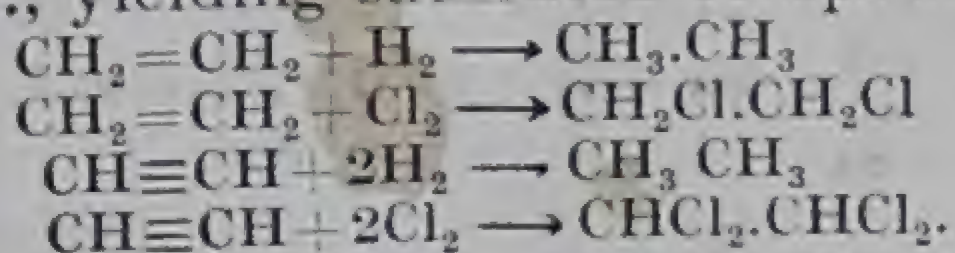
35. Metamerism. This term is rarely used nowadays. It refers to a kind of structural isomerism which exists between substances of the same class, and is due to the linking of different alkyl radicals to the same polyvalent atom or group. Metamerism is exhibited by ethers, ketones, esters, amines, etc. The following few cases may be mentioned as illustrations of this type of isomerism:—



36. Saturation and Unsaturation. If we compare the formula of ethane, $\text{CH}_3\cdot\text{CH}_3$, with that of ethylene, $\text{CH}_2=\text{CH}_2$, we shall observe that while in the former the four valencies of each of the carbon atoms are employed in forming *single* bonds between the various atoms, in the latter there exists a *double* linkage between the two carbon atoms. Similarly, in acetylene, $\text{CH}\equiv\text{CH}$, the two carbon atoms are linked together by a *triple* bond.

Compounds, like ethylene and acetylene, which contain one or more pairs of carbon atoms linked together by double or triple bonds are

termed *unsaturated*, while, as already stated, those in which all the carbon atoms are joined together by single bonds are said to be *saturated*. Since in the case of saturated compounds the maximum combining capacity of carbon atoms is already in action, they can form derivatives only by *substitution*. Unsaturated compounds, on the other hand, can form derivatives by direct *addition*. Thus ethylene and acetylene combine respectively with two and four atoms of hydrogen, chlorine, etc., yielding saturated compounds:—

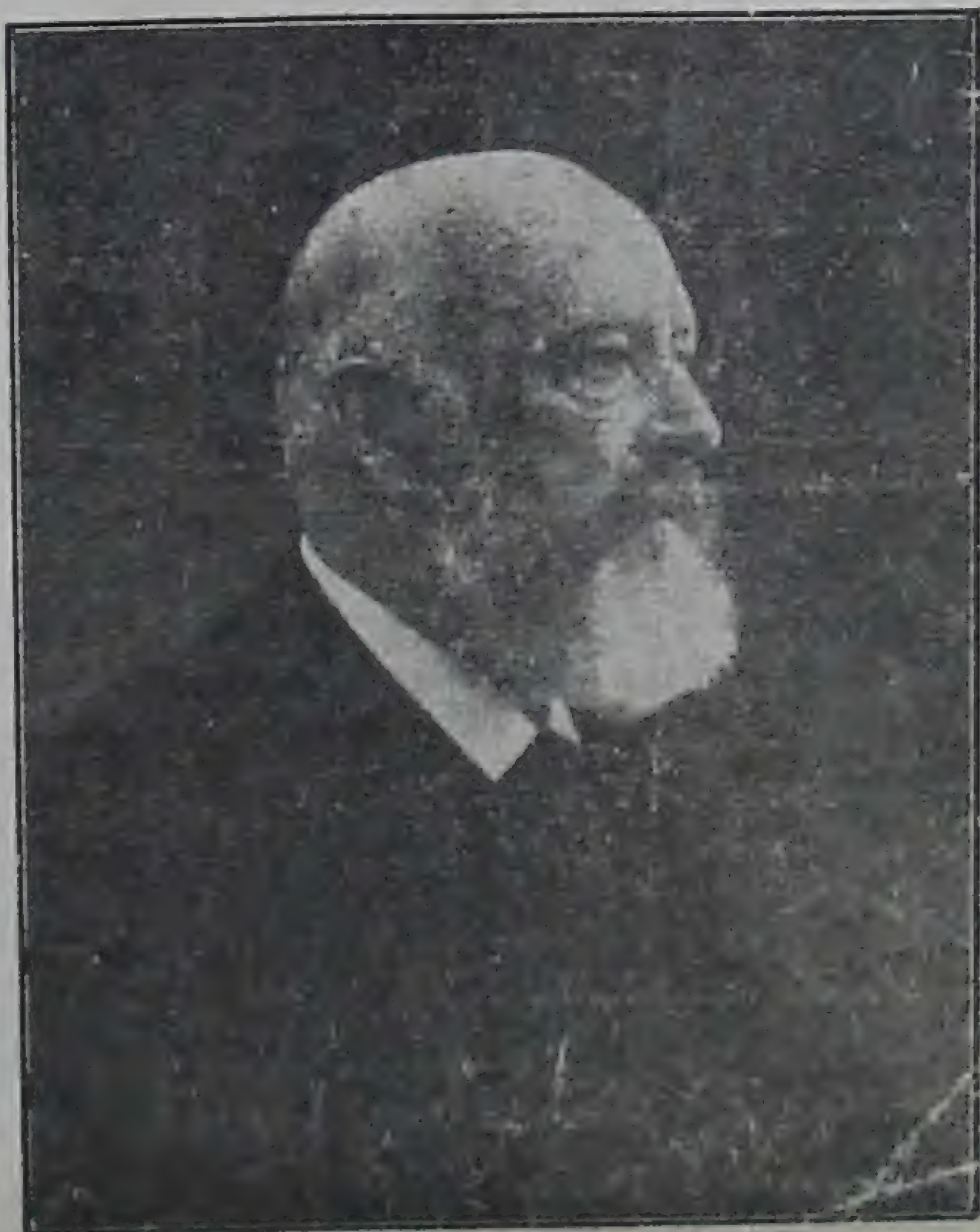


Thus, paradoxical as it may seem, carbon atoms bound together by double or triple linkages represent a more unstable state of affairs than singly bound carbon atoms. This singular behaviour has been explained by Baeyer by means of his "strain theory".

37. Baeyer's Strain Theory. According to the fundamental hypothesis of stereochemistry (Chapter VIII) the four valency bonds of the carbon atom are directed towards the angular points of a regular tetrahedron (at the centre of which the carbon atom is

**JOHN FRIEDRICH WILHELM
ADOLF VON BAEYER**
(1835—1917)

a German chemist, was born at Berlin. He studied chemistry under R. W. Bunsen and F.A. Kekulé, and in 1858 took his degree of Ph. D. at Berlin. In 1871 he was appointed professor of chemistry at Strassburg and five years later he migrated in the same capacity to Munich. He is well known as the founder of the Strain Theory (1885) and is responsible for the synthesis of indigo, though his method was found to be commercially impracticable. He also, worked on organic arsenic compounds, uric acid group, phthaleins, terpenes, and many other organic substances. He was awarded the Davy medal in 1881 by the Royal Society of London for his researches on indigo and the Nobel Prize in chemistry in 1905.



supposed to lie), and thus make an angle of $109^{\circ} 28'$ with each other. In 1885, Baeyer, pointed out that a single bond may be created between two carbon atoms without interfering with the line of action of any of the valencies of the two carbon atoms. There is, as we say, "free rotation about the single bond," *i.e.*, freedom of disposition of the six atoms or groups attached to the two carbon atoms.

On the other hand, when the two carbon atoms become doubly bound, the valencies concerned in the formation of the double bond are submitted to bending, or distortion. A definite strain is thus set up in the molecule, which renders the double bond easily attackable by reagents. The tension produced in the molecule by the creation of a double bond may be conveniently demonstrated by means of atomic models, in which the double bond is represented by a pair of flexible wires.

The mechanism of *addition reaction* that an unsaturated compound readily undergoes may be beautifully illustrated by means of atomic models, as in Fig. 33. The combination of ethylene (*A*) with bromine is here represented as being preceded by the *rupture* of the double bond, as shown at (*B*). The product of the reaction is dibromoethane (*C*), which is a saturated compound having normally directed valencies:

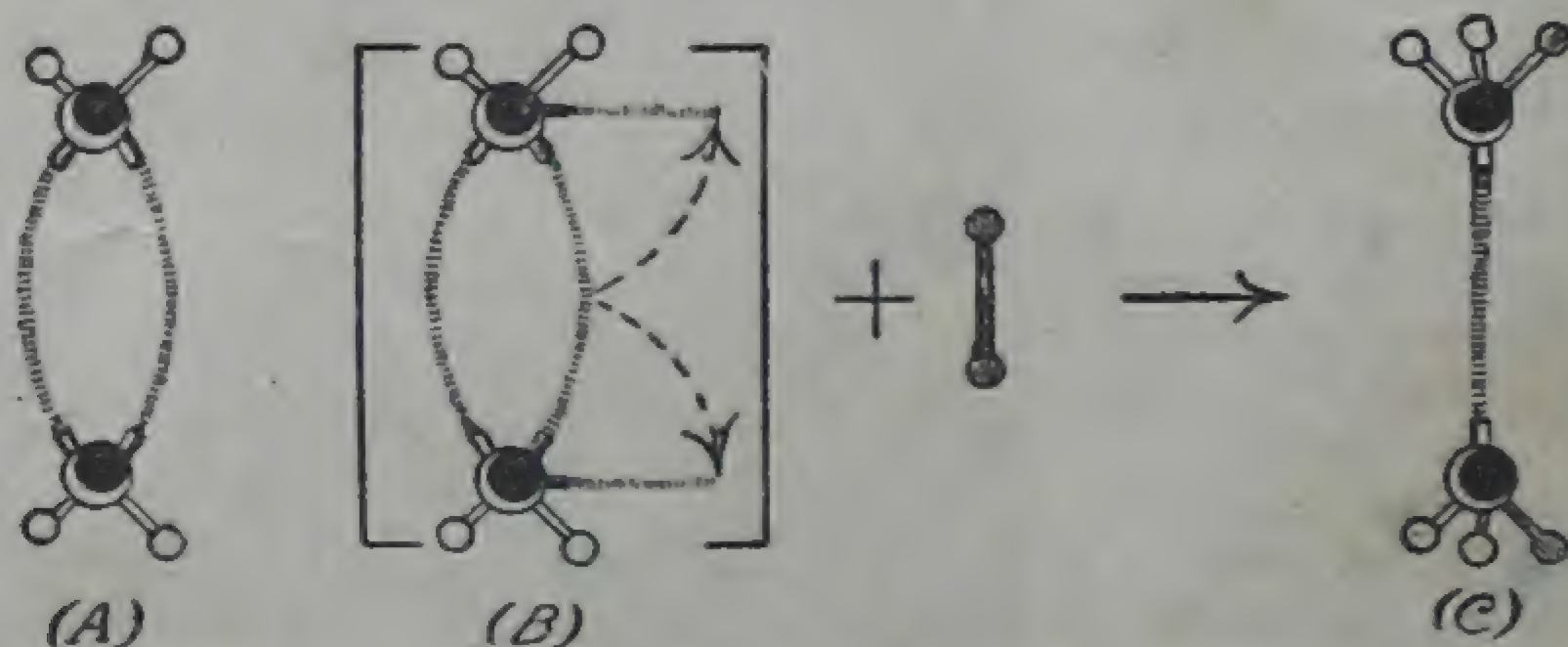


Fig. 33. Atomic-model Representation of the combination of Ethylene with Bromine.

The strain theory has been very helpful in explaining the relative stability of ring-systems having different number of saturated carbon atoms. The strain produced in each case is proportional to the angle of displacement of the valency bonds from their normal positions. It is possible to calculate this distortion in the various cases if we assume each axis to have undergone an equal displacement. Thus in



Fig. 34. Representation of Double bond by means of Atomic Models

$$\alpha = 109^{\circ} 28'$$

$$\beta = 54^{\circ} 44'$$

the trimethylene ring, $\text{H}_2\text{C} \begin{array}{c} \text{CH}_2 \\ \Delta \\ \text{CH}_2 \end{array}$, the carbon

atoms may be supposed to be at the corners of an equilateral triangle ABC (Fig. 35). The dotted lines AK and AL represent the original directions of the two valency bonds of the carbon atom A , and the curved lines their present disposition. The original angle, α , between the two bonds was $109^\circ 28'$, and the present angle between them is 60° . Hence, the deviation, β , undergone by each bond from its normal position

$$= \frac{1}{2}(109^\circ 28' - 60^\circ) = 24^\circ 44'.$$

Similarly, in the case of a double bond (see Fig. 34) the distortion is measured by the angle,

$$\frac{1}{2}(109^\circ 28' - 0^\circ) = 54^\circ 44'.$$

The following table gives the extent of distortion in different polymethylene rings, calculated as above:—

Double bond	+ $54^\circ 44'$	Penta-methylene	+ $0^\circ 44'$
Tri-methylene	+ $24^\circ 44'$	Hexa- ,,	— $5^\circ 16'$
Tetra- ,,	+ $9^\circ 34'$	Hepta- ,,	— $9^\circ 33'$

The pentamethylene ring, being under the least strain, is the most stable. Rings with less than five carbon atoms are progressively less stable and more reactive, until the exceedingly reactive double bond is reached.¹ The hexamethylene ring is nearly, though not quite, as stable as the pentamethylene ring.

The deductions of the strain theory are fully supported by experiment. In ethylene the strain is maximum and the tendency to form addition compounds resulting in the destruction of the ring is the highest. The strain is much less in the case of trimethylene, and hence the opening of the ring by means of bromine etc. here occurs much less readily than in ethylene (see Sec. 371 and Sec. 372). Again, whereas trimethylene carboxylic acid is readily attacked by hydrogen bromide in the cold, tetramethylene carboxylic acid is practically unaffected. Finally, pentamethylene carboxylic acids are not affected even on continued boiling with hydrogen bromide.

***38. Strainless Theory.** While the chemical behaviour of polymethylene compounds having a positive angle of deviation (*i.e.*, those having rings with 5 or less carbon atoms) agrees fairly well with Baeyer's strain theory, this is not the case with compounds having rings of 6 or more carbon atoms.

In the first place, the hexamethylene ring appears to be quite as stable as the pentamethylene ring; both classes of compounds refuse

¹ The ethylene linkage is evidently the limiting case of a polymethylene ring.

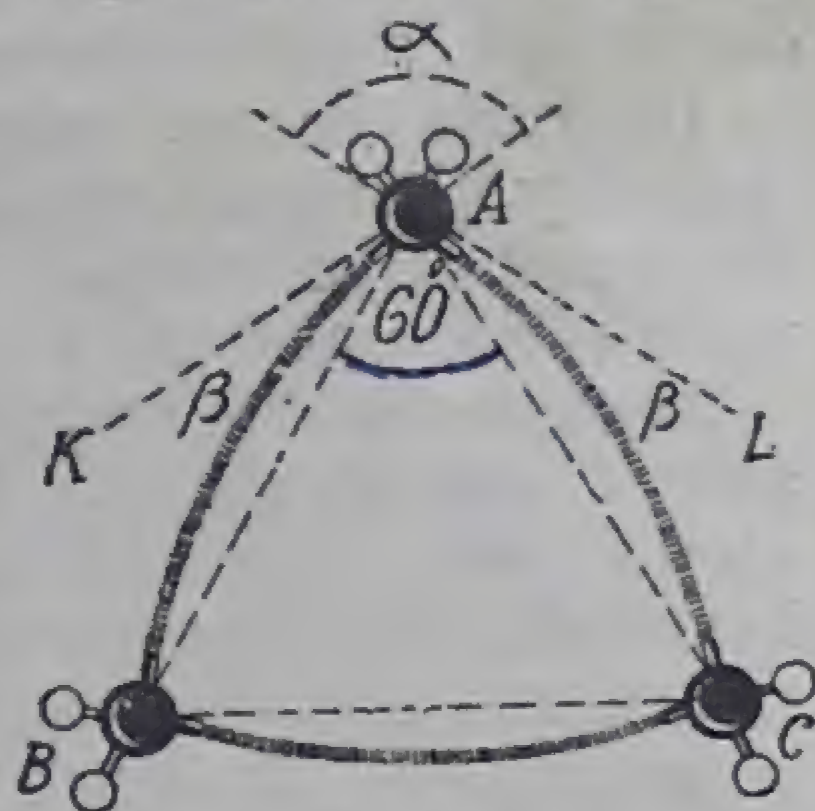


Fig. 35.
The Trimethylene Ring.
 $\alpha = 109^\circ 28'$; $\beta = 24^\circ 44'$

to react with bromine, hydrobromic acid, etc., and moreover, it is possible to convert a pentamethylene compound into a hexamethylene derivative, and *vice versa*. The heptamethylene ring should, according to Baeyer's theory, be quite as reactive as the tetramethylene ring. Actually, however, it is as stable as the pentamethylene and the hexamethylene rings. The same is true for rings containing 8 or more carbon atoms.

The remarkable stability of rings composed of 6 or more carbon atoms was explained by Sachse by assuming that all the carbon atoms composing such rings are *not* situated in the same plane. Thus hexamethylene is supposed to possess one of the space arrangements shown at I and II, (Fig. 36) and *not* the one shown at III. In the

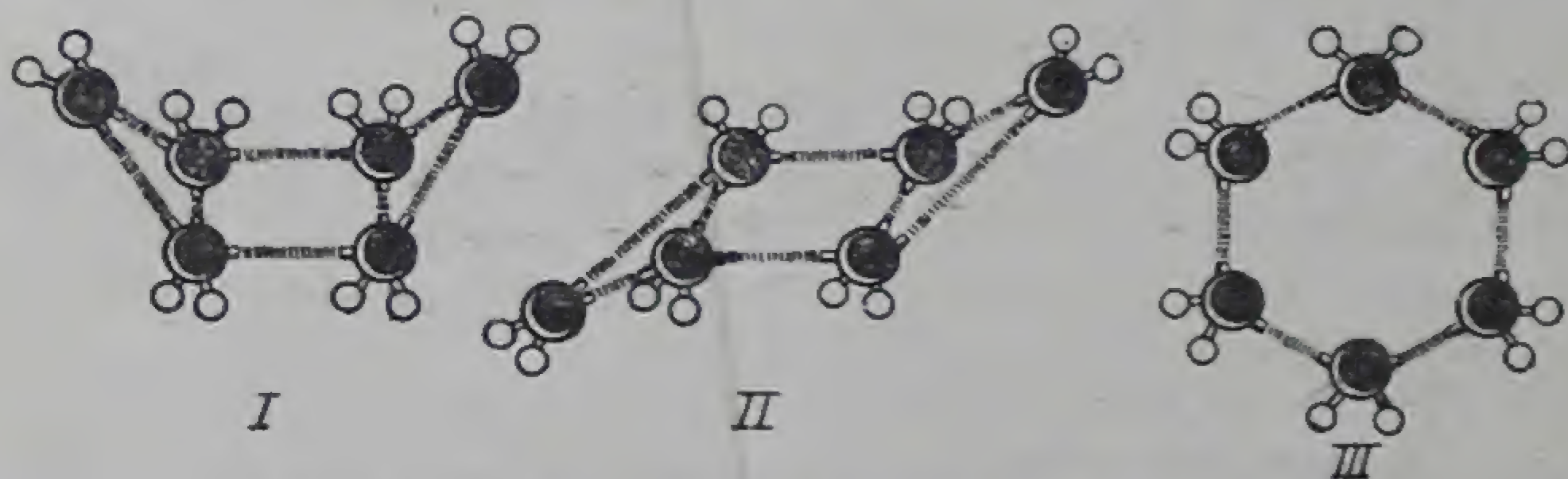


Fig. 36. Space Models for Hexamethylene.

last case all the carbon atoms are supposed to lie in the same plane, while in I and II they lie in two or three different planes.

Quite recently (1926), Ruzicka, a Swiss Chemist, has prepared cycloketones with ring-systems up to 30 carbon atoms, and has shown them to possess a high degree of stability. He points out that in such a case the ring, by virtue of its magnitude, is able to crumble up or twist itself into positions in which there is practically no distortion of the carbon linkages. Hence the molecule is free from any strain. The strongly odorous substances, muscone (from musk deer¹) and civetone (from civet cat²) are examples of this class of compounds. They have been shown to contain 15- and 17- membered rings respectively.

39. Thiele's Theory of Partial Valency. It was observed by Baeyer and Rupe in 1893 that when muconic acid,



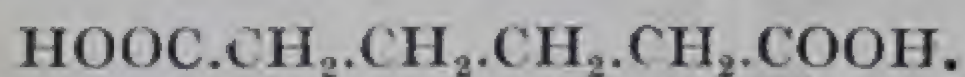
is reduced, four atoms of hydrogen are not added at once, as the existence of two pairs of double bonds might lead one to expect, but that only *two* atoms are first absorbed. These attach themselves

¹ Musk consists of the dried secretion of preputial follicles of the male musk deer found in the Himalayas.

² Found in Abyssinia.

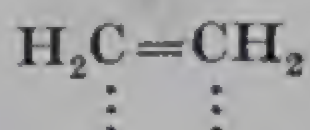
to the two carbon atoms carrying the carboxyl groups, and a new double bond comes into being between the two middle carbon atoms :
 $\text{HOOC.CH}_2.\text{CH}=\text{CH.CH}_2.\text{COOH}.$

The resulting compound, known as **hydromuconic acid**, on being further reduced, combines with two more atoms of hydrogen, yielding *adipic acid*,



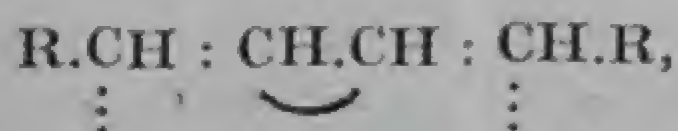
A system of alternating single and double bonds, as in muconic acid, is termed by Thiele **conjugated double bonds**. Many cases of 1 : 4 addition, as in muconic acid, have been observed in compounds containing conjugated double bonds.

In order to explain the peculiar behaviour of such compounds Thiele put forward the hypothesis that when two atoms are united by a double bond, the whole of the affinity between them is not used up, but that there remains a slight *residual affinity* or *partial valency* on each atom. This he denotes by dotted lines, *e.g.*,



He assumes that the power to form addition compounds is due to the presence of such residual affinities.

Now, in a system of conjugated double bonds there are four partial valencies : of these, the two middle ones are regarded by Thiele to have neutralized each other, while the other two remain active. This is usually denoted by the formula,



which explains the usual 1 : 4 addition in the case of compounds having a conjugated system of double bonds.

Thiele's theory appears to give a satisfactory explanation of the behaviour of a large number of unsaturated compounds. It has been particularly helpful in showing the saturated nature of the benzene ring (Part III). In recent years, however, facts have been discovered which do not agree with the rule of 1 : 4 addition.¹

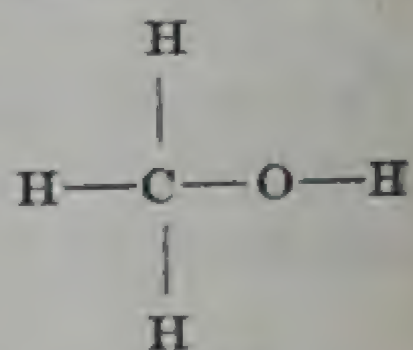
40. Determination of Structural Formula. After the molecular formula of a substance has been found as given in Chapter IV, the organic chemist proceeds to determine the structure of the molecule. This may involve the following steps :—

- (1) First, writing down all the possible combinations of the constituent atoms consistent with their respective valencies.
- (2) Then, from the various possible formulæ thus obtained selecting one that agrees best with the properties of the compound.

¹ See under Constitution of Benzene, Sec. 382.

In case the number of atoms in the molecule is small, the determination of its constitution is usually a simple matter. Thus, if the valencies of carbon, hydrogen and oxygen be assumed to be 4, 1 and 2 respectively, the compound having the molecular formula CH_4O (methyl alcohol) can have only one structure as shown in the margin. Similarly, the compound of the molecular formula CH_2O (formaldehyde) must have the structure $\text{H.C} \leq \frac{\text{H}}{\text{O}}$. In

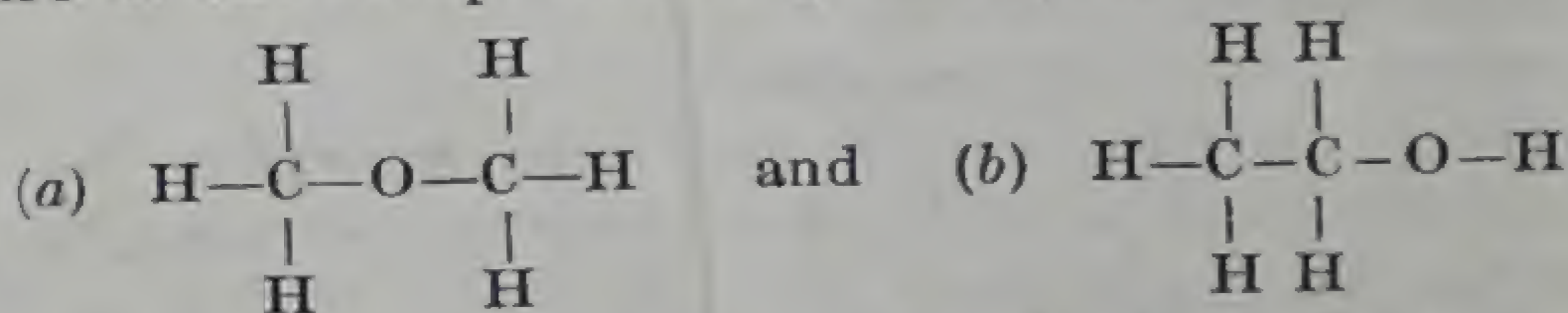
the determination of its constitution is usually a simple matter. Thus, if the



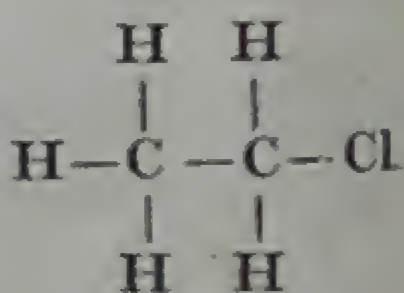
case two or more structural formulæ are possible, we must select the right one by reference to the following :—

(i) The possibility of the compound being transformed into, or of its being produced from, compounds of known structure. We know it from experience that *when an atom or radical present in a molecule is replaced by another substituent, the latter, as a rule, goes into the position originally occupied by the former.*¹

The procedure may be illustrated by reference to ethyl alcohol, $\text{C}_2\text{H}_6\text{O}$. As one may see by trial, there are only two ways in which the structure of the compound may be represented : viz.,



Now, ethyl alcohol may be obtained by the hydrolysis of ethyl chloride, $\text{C}_2\text{H}_5\text{Cl}$, and conversely, it may be converted into ethyl chloride by treatment with hydrogen chloride. Hence, its structure must be analogous to that of ethyl chloride. But there is only one structure possible for the latter substance, as shown in the margin. Hence, ethyl alcohol must possess the constitution (b) and not (a).

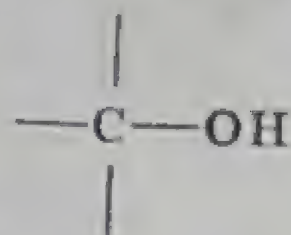


The conclusion thus arrived at is in complete harmony with the chemical behaviour of ethyl alcohol. Thus, of the six hydrogen atoms, that the molecule contains, only *one* is replaceable by sodium; hence this hydrogen atom must be in a different state of combination from the rest. This condition is fulfilled by the formula that we have just now selected.

(iii) The close similarity of the physical and chemical properties of the compound with those of another, whose constitution is known. Thus, an additional proof of ethyl alcohol as possessing the structure

¹In certain rare cases the atoms or radicals "migrate" to new positions. See, for instance, the *Walden Inversion*. Formation of resorcinol from benzene-o-disulphonic acid is another well-known example of the same phenomenon.

(b) is that in its entire physical and chemical behaviour it closely resembles methyl alcohol, for which there is only one structure possible, *viz.*, CH_3OH . Hence, ethyl alcohol must contain a hydroxyl group in its molecule, just as methyl alcohol does. Similarly, all other alcohols must have in their molecules the grouping shown in the margin.



(3) The formula finally adopted must be supported by as many reactions of the compound as possible. It must also be checked by reference to its various physical properties (See Chapter VI). As the last step, an attempt is made to *synthesize* the compound from one of known structure by a series of simple reactions that the formula under consideration may suggest. Should this be successful, the formula is finally accepted as established.

41. Tautomerism. A number of cases are known in which one and the same compound behaves as if it had *two* different structures. Thus, hydrocyanic acid may react as $\text{H}-\text{C}\equiv\text{N}$, or as $\text{H}-\text{N}\equiv\text{C}$. It gives rise to two different classes of alkyl derivatives, (i) the *cyanides*, derived from the first, and (ii) the *isocyanides*, derived from the second form. A substance which, like hydrocyanic acid can react according to two different structures is said to exhibit **tautomerism** (Gk. *tauto*, the same; *meros*, a part).

Tautomerism is thus a special kind of isomerism, where the two isomerides are represented by one and the same substance. According to the generally accepted view, which was first put forward by Baeyer, a tautomeric substance consists of a mixture of two labile forms in dynamic equilibrium with each other. For this reason, the term **dynamic isomerism** is sometimes used instead of tautomerism. The change of one form of tautomeric substance into the other is caused by the migration of a hydrogen atom from one polyvalent atom to another, and is accompanied by the necessary rearrangement of linkages. Thus in the case of hydrocyanic acid the change from one form into the other occurs as follows:



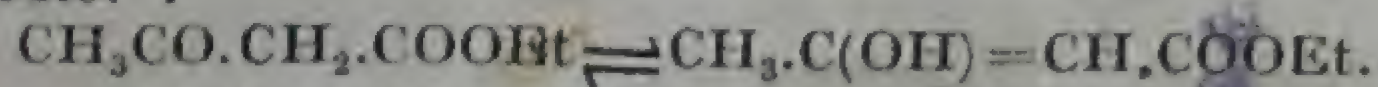
On account of the change of linkage involved in the transformation of one form of a tautomeric substance into the other, the phenomenon is sometimes termed **desmotropism** (Gk. *desmos*, a bond; *tropos*, turn).

Of the many known examples of tautomerism, mention may also be made of the following:

Cyanic acid:



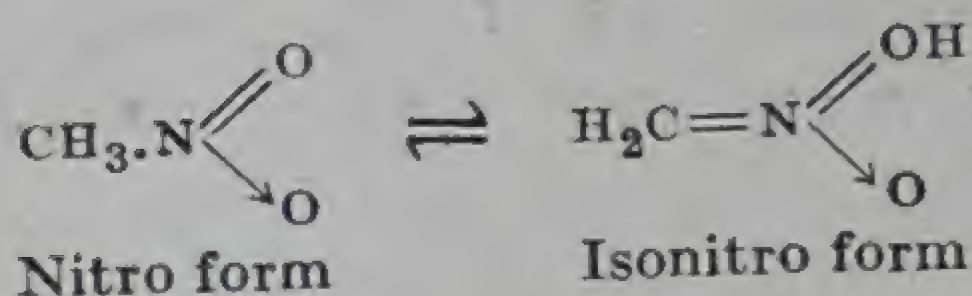
Aceto-acetic ester:



Keto form

Enol form

Nitro-methane :



42. Electronic Theory of Valency. According to the modern views, the atom is a complex structure. At the centre of the atom is the positively charged nucleus, surrounded by negatively charged particles, which keep revolving round the positive centre. The negatively charged particles are called electrons. They are the common constituents of all atoms. The nucleus of the atom is not an elementary particle but a composite structure, made up of neutrons and protons, and forms a very small part of the volume of the atom.

The electron carries a single elementary negative charge, (the smallest possible charge that can exist by itself) and possesses an exceedingly small mass, being $1/1840$ of that of the hydrogen atom.

The proton carries a single elementary positive charge (equal and opposite in kind to that of the electron). The proton has a mass practically equal to that of the hydrogen atom. The neutron carries no charge, but has a mass very nearly equal to that of the proton. Since the atom is electrically neutral, the number of protons in the nucleus of the atom is equal to the number of electrons outside the nucleus. The charge on the nucleus, being equal to that of the total number of the protons in the nucleus, is known as the nuclear charge. The electrons outside the nucleus keep continually revolving round the nucleus in circular or elliptical orbits in the same way as the planets in the solar system revolve round the sun. Hence they have often been referred to as the "planetary electrons".

The number of these planetary electrons (or the number of protons in the nucleus)) is termed the atomic number of the element, and forms the basis of the classification of the elements.

The number of electrons in each orbit corresponds to the condition of maximum electrical stability. The atomic structures of the elements that commonly occur in organic compounds are given in Fig. 37, the nucleus in each case being represented by the sign +.

The chemist is concerned almost exclusively with the electrons present in the outermost orbit. These are called valency electrons, as the valency of an element depends on these. Excepting the elements of Group 0 and VIII, the number of valency electrons corresponds to the group in the periodic table to which the element belongs. The outermost orbit of helium (atomic number 2) contains a maximum of 2 electrons; all the other members of zero group have a complete outer orbit of 8 electrons. In case the outermost orbit

is incomplete, the atom has a tendency to borrow, lend, or share electrons in order to have a complete outer orbit similar to that of the nearest member of the helium family. This tendency of the atom is the cause of chemical combination.

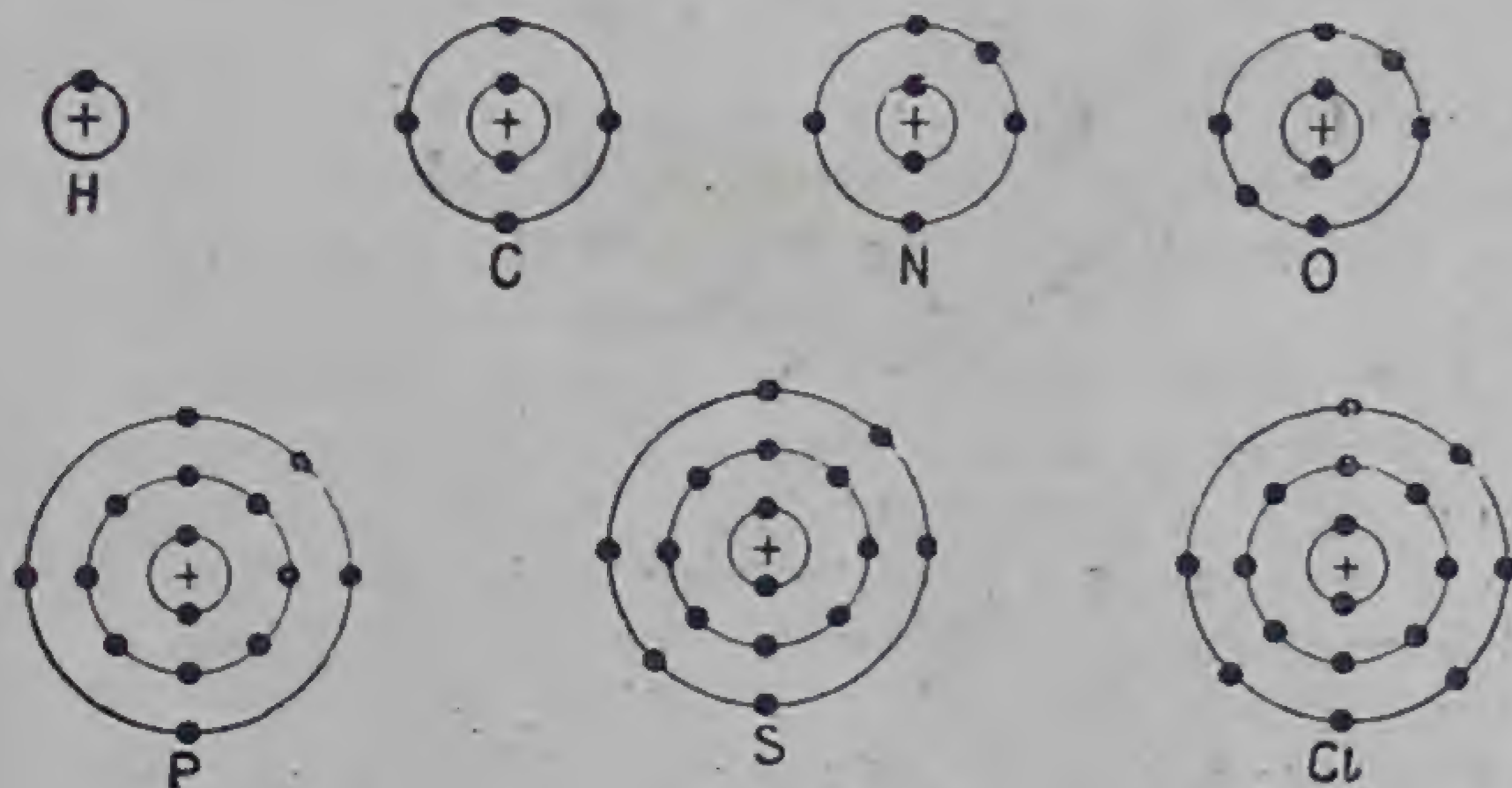
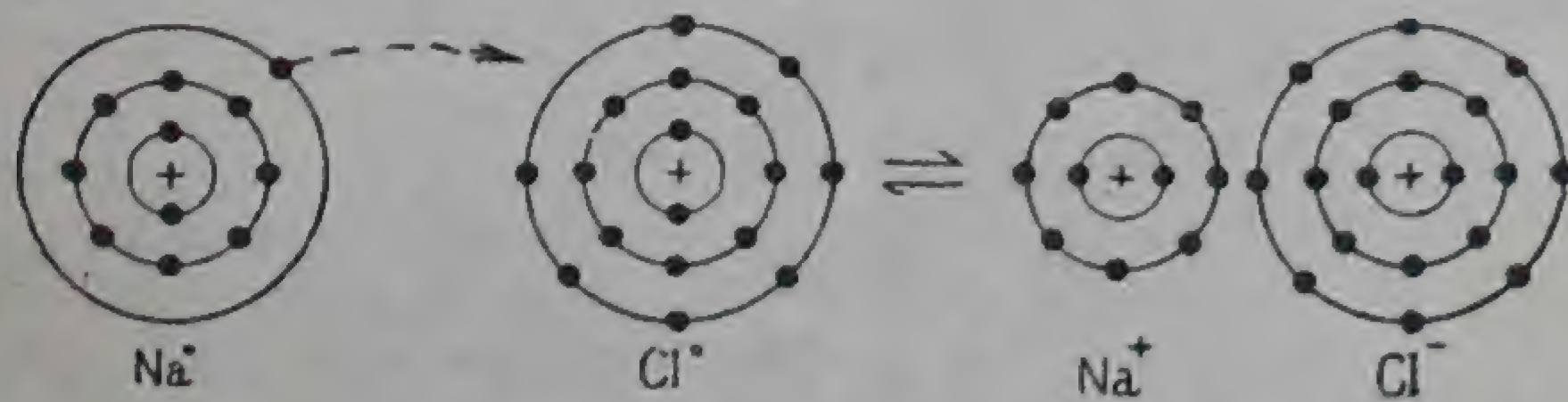


Fig. 37. Atomic structure of Elements occurring in Organic Compounds.

A chemical combination between atoms is of the following three types:

- (1) Electrovalency,
- (2) Covalent linkage.
- (3) Co-ordinate linkage.

(1) **Electrovalency.** Union between two atoms may take place by the *transfer* of electrons from the outermost orbit of the one to that of the other. Thus when a chlorine atom having 7 valency electrons combines with a sodium atom having 1 valency electron, the electron, from the latter atom is transferred to the chlorine atom. Both the atoms now have a stable arrangement of 8 electrons in their outermost orbits. Further, the transfer of an electron from the sodium to the chlorine atom makes the former acquire a unit positive charge, and the latter a unit negative charge. These charged atoms or *ions* hold each other by mutual attraction :

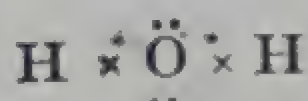


The change is most conveniently represented as follows : —

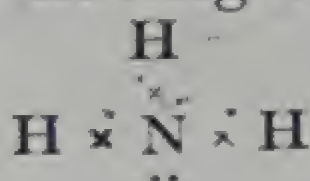


A compound formed as above is termed an **electrovalent compound** or **polar compound**. The latter name refers to the fact that the molecule of such a compound has a positive and a negative pole, and consequently, under suitable conditions, has a tendency to break up into positive and negative ions. The combination of the above type, called an **electrovalency**, is found chiefly among acids, bases and salts.

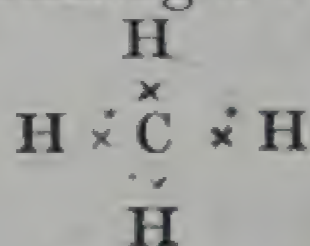
(2) **Covalent Linkage**. This type of linkage is especially prevalent among organic compounds. In this case the atoms undergo combination by *sharing* one, two or three pairs of electrons with each other so as to complete their octets. In each pair of shared electrons one is contributed by each atom. One pair of shared electrons corresponds to a *single* bond, two pairs to a *double* bond, and three pairs to a *triple* bond. A covalent bond is non-ionizable. The following are some examples of compounds having covalent linkages:



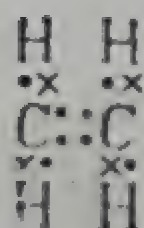
Water



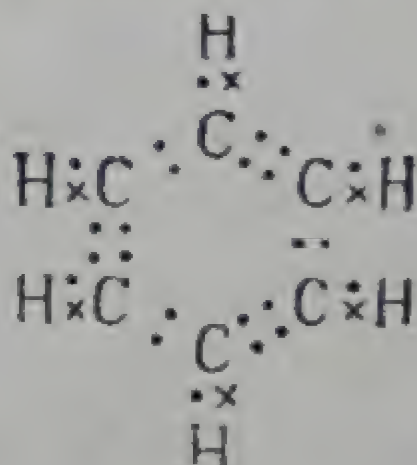
Ammonia



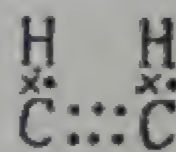
Methane



Ethylene



Benzene

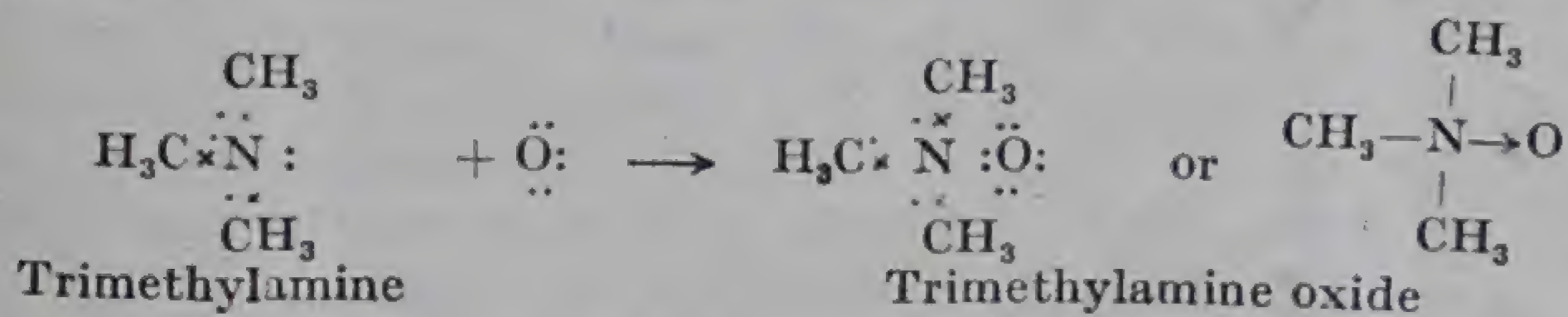


Acetylene

(3) **Co-ordinate Link or Semi-polar Bond**. This form of linkage is similar to the covalent link except that *both* the electrons constituting the bond are supplied by *one* of the atoms. Sidgwick calls this a *co-ordinate link*, since he has shown it to exist in Werner's co-ordinate compounds.

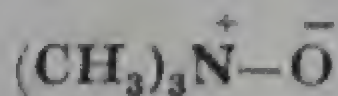
A necessary condition for the formation of a co-ordinate link is that one of the atoms, called the **donor**, must have at least one **lone pair** of valency electrons, *i.e.*, those not concerned in union with any other part of the molecule, while the other atom, called the **acceptor** must require these electrons to complete its octet. Many atoms, even in the state of combination, have one or more lone pairs of electrons. Thus nitrogen in ammonia has one such pair and oxygen in water has two (though only one of these is regarded as effective). A "covalently saturated" molecule like CH_4 or C_2H_6 cannot provide a donor, since all its valency electrons are shared.

In the formation of co-ordinate link, the donor retains the number of its valency electrons unchanged, while the acceptor increases its own number by two. A simple example of the formation of co-ordinate link is that of trimethylamine oxide. In trimethylamine, $(\text{CH}_3)_3\text{N}$, as in ammonia, the nitrogen atom has a lone pair of electrons, while the oxygen atom requires a pair of electrons in order to complete its octet. Hence the change may be represented as follows :—

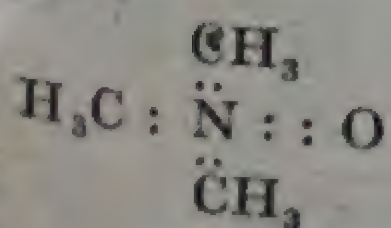


In the second of the above pair of formulæ of trimethylamine oxide a simple co-valency is represented by a single line and a co-ordinate link by a short arrow. The single line of the arrow indicates that the link is formed by the sharing of two electrons and the direction of the arrow shows that both the electrons are provided by the nitrogen atom. This mode of representing a co-ordinate valency is due to Sidgwick.

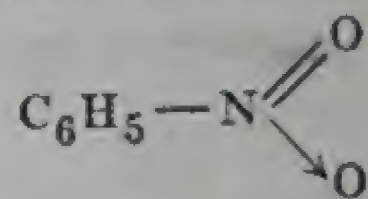
Lowry, who first proposed the above electronic formula for the amine oxides, is of the opinion that the formation of a link like this necessarily implies that the molecule has developed polarity. The nitrogen atom has acquired a positive charge because of its two electrons getting further away from it than prior to the combination, while the oxygen atom acquires a negative charge, because it has received two additional electrons. Hence the two parts of the molecule will be held together not only by the sharing of a pair of electrons, as in a single covalent bond, but also by their mutual electrical attraction. For this reason, Lowry calls this type of linkage **semi-polar bond**, and indicates its nature by placing the signs + and — against the donor and the acceptor atoms respectively. Thus the structure of trimethylamine oxide is represented as under :



In the older formula of the amine oxides, $\text{R}_3\text{N}=\text{O}$, the presence of a normal double bond was assumed. This is, however, untenable, since if we translate it into the electronic formula we must assume the nitrogen atom to possess a valency group of ten electrons (see margin), which, as we know, is an unstable arrangement. The new formulation is justified by the evidence of Sugden's parachor (Chapter VI).

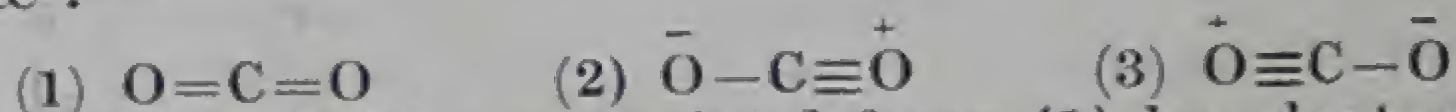


Sugden has shown that most of the double bonds of structural organic chemistry are true double covalent bonds. The nitro group, —NO_2 , however, appears to possess one true bond together with one semi-polar bond, or co-ordinate link. Nitrobenzene, therefore, is assigned the electronic formula given in the margin.



***43. Mesomerism or Resonance.** It has been established with the help of wave mechanics that if a molecule can be represented by two (or more) different structural formulæ, then its actual state is represented neither by the one formula nor the other, nor yet by a mixture of the two forms as in the case of tautomeric substances; it is in fact a hybrid structure intermediate between the two formulæ. The phenomenon is termed *mesomerism* or *resonance*. The mesomeric state of the molecule possesses a minimum of energy and, therefore, a maximum of stability. For mesomerism to be possible, two conditions must be satisfied: First, the position of the atoms in the two structures must be *approximately* the same; secondly, the energies of formation of the two forms and, therefore, their stabilities must not be much different.

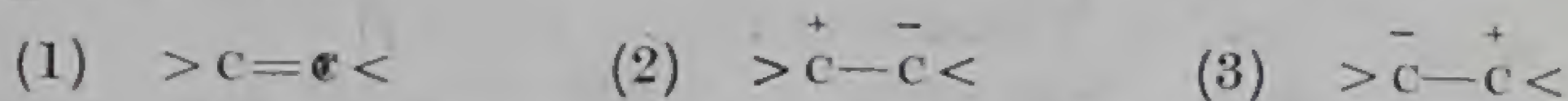
The carbon dioxide molecule presents one of the simplest examples of mesomerism. It may be represented by any of the following three formulæ:—



The structures (2) and (3) are derived from (1) by electronic displacement. The distances between the oxygen atoms for the three formulæ, as calculated theoretically, are very nearly identical (about 2.56 \AA^1). The energy of formation of each form is very nearly 350 kilo-cals. Hence the two necessary conditions for mesomerism, *viz.*, similarity in nuclear positions and in energy content, are fulfilled. The experimental value of the distance between the oxygen nuclei is 2.30 \AA and of the heat of formation of carbon dioxide 380 kilo-cals. The interatomic distance, therefore, is somewhat less and the energy content appreciably less than the calculated values for any of the three forms. This is in agreement with the predictions of wave-mechanics. We, therefore, see that the carbon dioxide molecule is actually represented by none of the above three structures but by a mesomeric state of lower energy content. This state is generally denoted by the mesomeric formula $\text{O} \text{---} \text{C} \text{---} \text{O}$.

¹ The *Angstrom unit* (denoted by \AA) is employed in expressing wavelengths of different radiations and distances between atoms in a molecule. It is equal to 10^{-8} cm .

Another interesting example of resonance is furnished by ethylene, which has been shown to exist in the mesomeric state between the following three forms :—



Since the stability of structures (2) and (3) is diminished by their dipolar character, the mesomeric state is much nearer to the non-polar form (1). At the time of reaction, however, the transformation of the non-polar into one of the polar forms occurs. It is on the basis of this polar activation of the double bond that the addition reaction of ethylene and other unsaturated substances are generally explained.

The phenomenon of mesomerism is of considerable interest at the present time, and has been successfully employed in the elucidation of the behaviour of a number of molecules and groups, such as the nitro-group, the carbonyl group, the carboxylate ion, the azide ion, the benzene ring, etc.

QUESTIONS

1. Give the different steps in the systematic investigation of the formula of an organic compound. (Punjab, Inter., 1927)
2. What do you understand by Isomerism? Name the different classes of isomerism met with in organic compounds.
3. Write an account of Kekulé and Couper's theory of molecular structure.
4. How would you prove the equivalence of the four valencies of the carbon atom? Why do we assume a tetrahedral configuration of the carbon atom? (Punjab, B.Sc., 1939)
5. What are the chief classes of organic compounds? On what is the classification based?
6. Distinguish between *nuclear isomerism*, *position isomerism*, and *metamerism*. Give illustrative examples.
7. Write short notes on (a) homologous series, (b) substitution, (c) saturation.
8. What do you understand by 'unsaturation' in organic compounds? What reactions are characteristic of this state? (Punjab, Inter., 1920)
9. Write a note on "Baeyer's Strain Theory." (Punjab, B.Sc., 1929, 1931; B.Sc., Hons. School, 1929)
10. What is the theory of strain? Discuss Thiele's theory of partial valency. (Punjab, B.Sc., 1941)
11. Write a short note on 'conjugated double bonds.' (Punjab, B.Sc., 1925)
12. Show how the constitution of an organic compound can be determined by its chemical behaviour and synthesis. (Punjab, B.Sc., Hons. 1926)
13. Write a note on Tautomerism. Give at least three examples of substances showing this phenomenon.
14. Write an essay on the 'Electronic Theory of Valency'.
15. Write a note on the phenomenon of mesomerism.

*Not in the
course*

CHAPTER VI

RELATION BETWEEN PHYSICAL PROPERTIES AND CHEMICAL CONSTITUTION

In recent years the study of physical properties of organic compounds has become considerably important chiefly in connection with the elucidation of their chemical constitution. From this point of view the physical properties discussed below are especially helpful to the chemist.

44. Parachor. An additive property recently investigated by Sugden, and termed by him the *parachor* has proved very useful for having an insight into the constitution of the molecule. For a non-associated liquid, the value of the parachor $[P]$ is constant and is given by the expression

$$[P] = \frac{M\gamma^{\frac{1}{4}}}{D-d}$$

where M is the molecular weight, γ the surface tension, D the density of the liquid and d the density of the vapour.

As is evident from the above expression, parachor is to be regarded as *molecular volume*, M/D , which has been corrected, with the help of the surface tension, for the effect of the very great internal pressure of liquids. In this way the value is made independent of the temperature at which it is measured.

The parachor has been shown to be an additive property of a simple type, and is made up of two series of constants, one for the atoms and the other for the linkages present in the molecule. For isomeric substances whose constitutions differ only in the position of groups or linkages in the molecule, the parachors are found to be identical. The following examples illustrate this fact:—

PARACHORS OF SOME ISOMERIC ESTERS

Methyl valerate	292.5
Ethyl butyrate	293.6
<i>n</i> -Propyl propionate	295.3
<i>i</i> -Butyl acetate	295.1
<i>i</i> -Amyl formate	293.6

PARACHORS OF ISOMERIC XYLENES

<i>o</i> -Xylene	283.3
<i>m</i> -Xylene	283.8
<i>p</i> -Xylene	283.8

(a) **Atomic Parachors.** Sugden by comparing the parachor values for successive members of a homologous series, calculated a mean constant difference for CH_2 . For instance, the observed parachors for ethane, C_2H_6 , and decane, $\text{C}_{10}\text{H}_{22}$, are respectively 111.0 and 424.2. Hence the mean value for CH_2 is $\frac{424.2 - 110.0}{8}$ or 39.0. From this the parachors for carbon and hydrogen can be calculated as follows:—

$$\text{Parachors for decane, } \text{C}_{10}\text{H}_{22} = 424.2$$

$$\text{Parachor value for } 10 \times \text{CH}_2 = 390.0$$

$$\therefore \text{Parachor for } 2\text{H} = 34.2$$

$$,, \quad ,, \quad \text{H} = 17.1$$

$$,, \quad ,, \quad \text{C} = 39.0 - 34.2 = 4.8$$

Similarly, the parachor values for other elements can be calculated from the parachors of saturated aliphatic compounds.

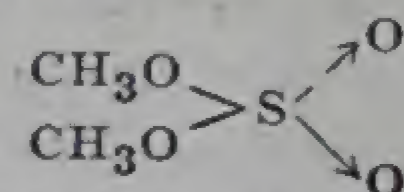
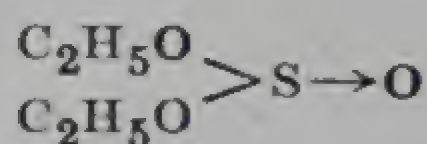
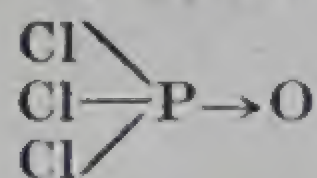
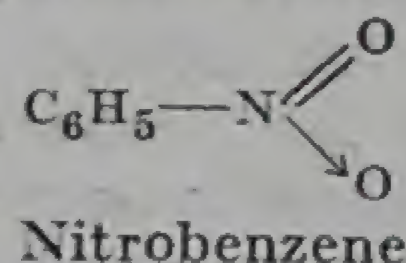
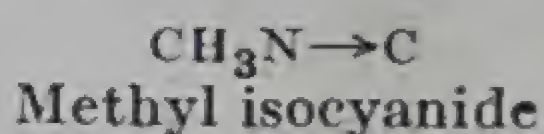
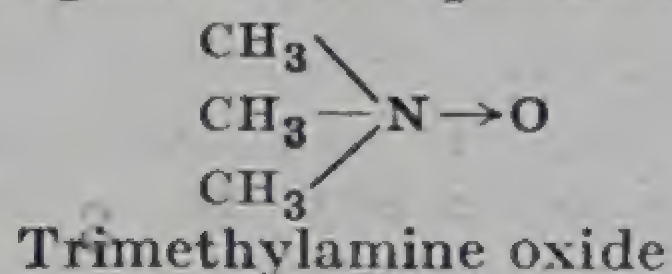
(b) **Structural Parachors.** In all saturated compounds the parachor of the single covalent bond is arbitrarily taken as zero. If we compare the parachors of saturated open-chain hydrocarbons with those of unsaturated and cyclic types, we find that a definite contribution is made by each double bond, triple bond, and 3-, 4-, 5-, 6-membered ring that the molecule may contain. Some of the atomic and structural parachors thus deduced are tabulated below:—

C ...	4.8	Double bond ...	23.2
H ...	17.1	Triple bond ...	46.6
O ...	20.0	3-membered ring ...	16.7
N ...	12.5	4- ,, ,, ...	11.6
S ...	48.2	5- ,, ,, ...	8.5
P ...	37.7	6- ,, ,, ...	6.1
Cl ...	54.3	Semi-polar double bond ...	1.6
Br ...	68.0	O_2 in esters ...	60.0

It has been found that the parachor value for the double bond is independent of the nature of the atoms linked, and is the same for the links $\text{C}=\text{C}$, $\text{C}=\text{O}$, $\text{C}=\text{S}$, $\text{C}=\text{N}$, and $\text{N}=\text{O}$. Similarly, the value for the triple bond in nitriles and acetylene and its derivatives is the same, *viz.*, 46.6, which is almost exactly twice the value for a double bond. Hence, it is not possible to distinguish between compounds such as $\text{CH}_3\text{O.C}\equiv\text{N}$ and $\text{CH}_3\text{N}=\text{C}=\text{O}$ by a parachor determination.

Sugden found that of the compounds formerly supposed to contain a double bond, the majority gave the parachor value for the double bond of +23.2, while a few gave a small negative value of -1.6. On attempting to write the electronic formulæ of these latter compounds using a double covalent linkage, it was found that this could only be done by breaking the octet rule and assigning to one of the atoms taking part in the double bond a valency group of 10 or more

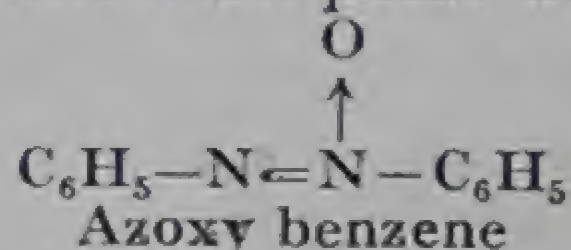
electrons. In all such cases, it is possible to preserve the octet rule by writing the double linking as a semi-polar double bond (see Sec. 42). Examples of compounds containing semi-polar double bond are :



The parachor determination of benzene and a large number of its derivatives shows that the molecule contains three normal double bonds as formulated by Kekulé. Thus the value for benzene is found to be 206.2, and as calculated theoretically it should be 207.1.

6C	$6 \times 4.8 = 28.8$
6H	$6 \times 17.1 = 102.6$
3 double bonds	$3 \times 23.2 = 69.6$
6-membered ring	$= 6.1$
Total	$= 207.1$

Similarly, azoxy compounds have been shown to contain one normal double bond and one semi-polar double bond.



45. Molecular Refraction. Landolt examined the molecular refractions of members of several homologous series and concluded that, in general, molecular refraction is an *additive* property, being, in the case of a given compound, equal to the sum of the atomic refractions of the component elements. In the following table are given some of the more important atomic refractions as referred to the α -line in the hydrogen spectrum:—

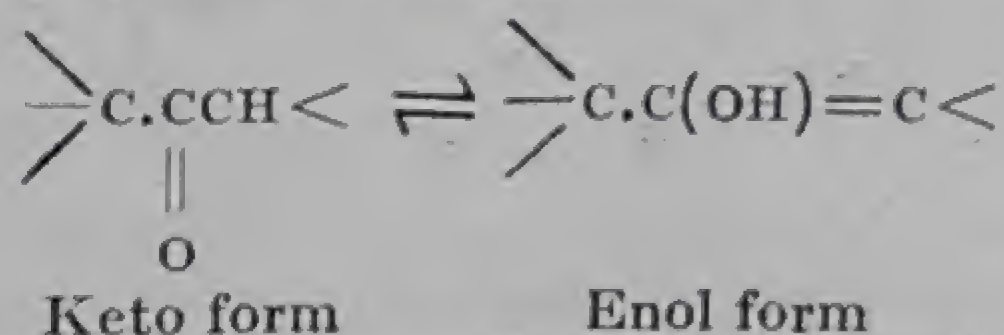
Element	Atomic Refraction
Carbon in single bond	2.365
Hydrogen	1.103
Oxygen in hydroxyl group	1.506
Oxygen in carboxyl group	2.328
Oxygen in ethers	1.655
Chlorine	6.014
Bromine	8.863
Iodine	13.808
Ethylene bond	1.836
Acetylene bond	2.220

As is clear from the above table, the molecular refraction is not purely additive, but to a certain extent constitutive. Thus the atomic refractions of carbon, oxygen, and other polyvalent elements depend on the state of combination. Hence the molecular refraction determination may be employed to elucidate the chemical constitution of a compound. Thus the observed molecular refraction of benzene, referred to the α -line in the hydrogen spectrum, is 25.93 which points to the presence of three double bonds in the ring, as in Kekulé's formula. This is in fair agreement with the calculated value of 26.3

$$\begin{array}{rcl} 6\text{C} & = & 14.2 \\ 6\text{H} & = & 6.6 \\ 3 \text{ double bonds} & = & 5.5 \\ & & \hline & & 26.3 \end{array}$$

The determination of refractivity has been helpful in clearing up the constitution of several organic compounds, *e.g.*, thujone, isopinone, α - and β -terpinene, and camphene.

The refractivity determination has been employed for the study of the keto-enol type of dynamic isomerism :



We see that the change from the keto to the enol form involves the creation of an ethylene bond and a change from $>\text{C}=\text{O}$ to

$\diagup \text{C}-\text{O}-$. The former means an increase of 1.836 units and the

latter a decrease of 0.822. The change is, therefore, accompanied by a net increase of 1.014 units. Hence, if the molecular refractivity is found to be about 1 unit higher than the theoretical value for the keto form, we infer the presence of a preponderating amount of the enol form. Thus in the case of aceto-acetic ester the observed molecular refraction for the α -line is found to be 31.89. The values calculated for the ketonic and enolic formulæ are respectively 31.5 and 32.5.

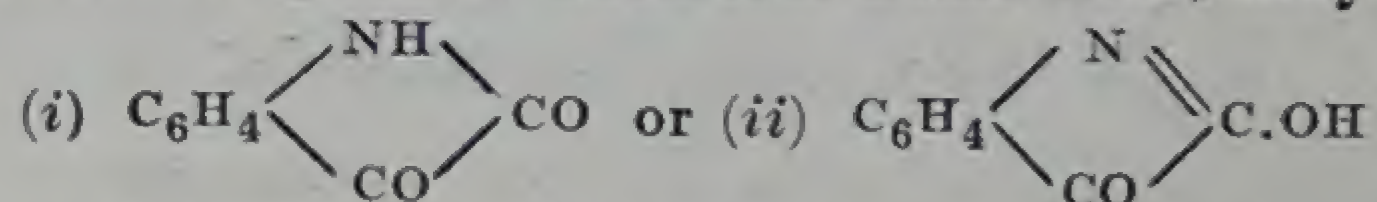
KETONIC FORM	
$\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{OC}_2\text{H}_5$	
6C	= 14.2
10H	= 11.0
2O (carbonyl)	= 4.6
1O (ether)	= 1.7
	<hr/>
	31.5

ENOLIC FORM	
$\text{CH}_3 \cdot \text{C}(\text{OH})=\text{CH} \cdot \text{CO} \cdot \text{OC}_2\text{H}_5$	
6C	= 14.2
10H	= 11.0
1 (ethylene bond)	= 1.8
1O (carbonyl)	= 2.3
1O (ether)	= 1.7
1O (hydroxyl)	= 1.5
	<hr/>
	32.5

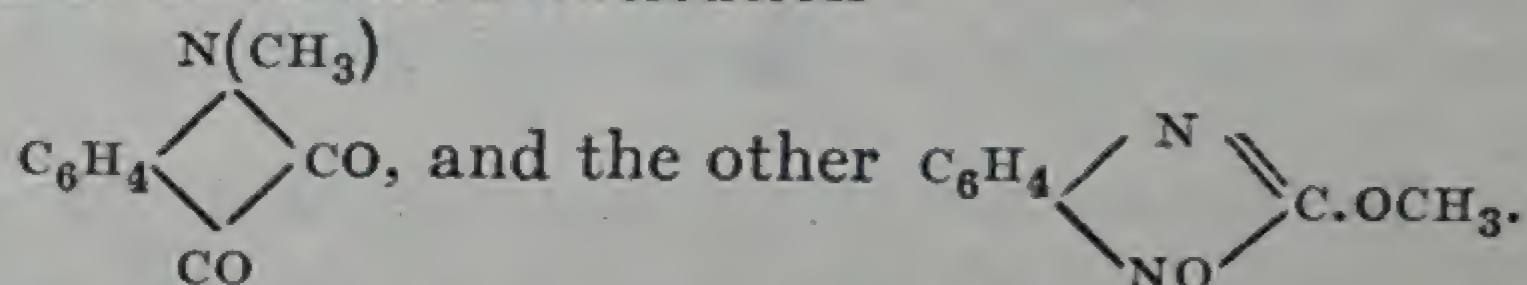
It thus follows that ethyl acetoacetate at the ordinary temperature consists mainly of the keto form with a small proportion of the enol form.

46. Absorption Spectra. If a beam of ordinary light is allowed to pass through a solution of a coloured substance, a part of the light is absorbed, and dark absorption bands appear in the spectrum. Further, it is found that the absorption is not confined to the visible part of the spectrum; it extends to the ultra-violet and the infra-red regions. As yet, little is known of the relation of the infra-red absorption to chemical constitution, while the absorption in the visible and the ultra-violet regions has been helpful in the elucidation of the structure of a number of compounds. The absorption in the visible and the ultra-violet regions can be detected by means of photographic plates. Hartley and other investigators have shown that, as a rule, substances of similar constitution give similar absorption spectra.

One of the most important examples of compounds whose structure has been elucidated with the help of absorption spectra is that of isatin, which, according to its chemical behaviour, may be either

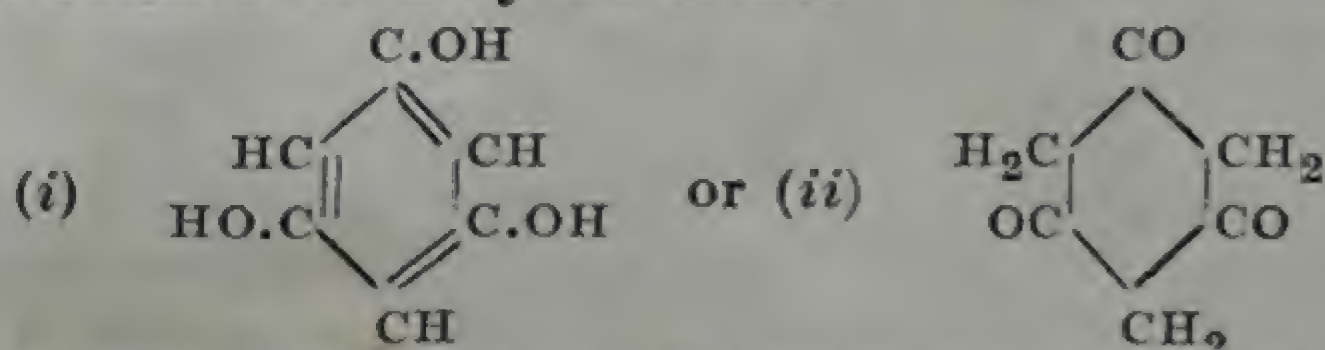


Now, there exist two methyl derivatives of isatin. One of these has been shown to have the constitution



Hartley and Dobbie, in 1899, compared the absorption spectra of these two compounds with that of isatin, and found that the latter was closely similar to that of the *N*-methyl derivative and was quite different from that of the other isomer. Hence, it was concluded that isatin must have the constitution represented by formula (i) given above.

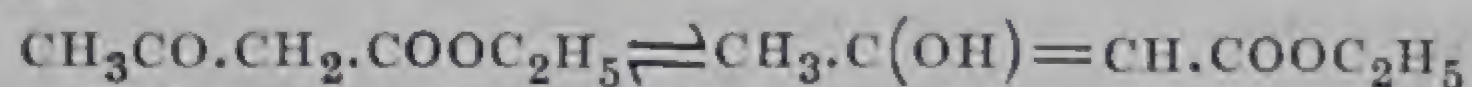
Another interesting case is that of phloroglucinol which according to its chemical behaviour may be either



Hartley, Dobbie and Lauder found that the absorption spectrum of the compound is similar to that of its trimethyl ether, $\text{C}_6\text{H}_3(\text{OCH}_3)_3$,

which, of course, can have only the phenolic structure. Hence they concluded that, when in the free state, phloroglucinol possesses the structure of a true phenolic compound [formula (i)].

Another example is that of ethyl acetoacetate which exhibits *keto-enol tautomerism* :—



The spectrum of the ester is found to possess no bands, whereas its metallic derivatives show a strongly banded absorption. Further, the addition of an alkali to the ester causes a banded spectrum to appear which becomes more and more prominent as the quantity of the alkali added is increased. Now, the metallic derivatives of the ester must be regarded as being derived from the enolic form. Hence the ester itself must consist mainly of the *ketonic* form.

QUESTIONS

1. Explain the term *parachor*. To what use has the *parachor* determination been put by the organic chemist? Give illustrative examples.
2. Write a short essay on the relation between physical properties and chemical constitution. (Punjab, B.Sc. Hons., 1924)
3. "The chemical constitution of some substances can be determined from a study of certain physical properties." Justify this statement. (Punjab, B.Sc. Hons., 1931)
4. Give an account of the application of molecular refraction in the study of chemical constitution.
5. Write a short account of the application of absorption spectra in the elucidation of molecular structure. Give illustrative examples.

CHAPTER VII

OPTICAL ACTIVITY AND POLARIMETRY

47. Polarization of Light. To understand the phenomenon known as "Polarization", we may take the following illustration: Suppose we have a tightly stretched string knotted near the middle. The knot is free to move in any direction at right angles to the string. Hence, if we pluck the string, the knot will be found in all probability to describe a series of figures varying between a circle and a straight line. Every point on the string, will, of course, be vibrating in a similar manner. Now, suppose that we take a card in which a slit has been cut, slip it on to the string near the knot, and pluck the string once again. This time the knot will be found to vibrate only in one direction, namely the direction of the slit. Suppose that we now take another piece of card with a slit cut in it, and slip it on to the string near the first card. We shall then see that the knot can vibrate only when the slits lie parallel to each other: if the two slits lie at an angle, the string is gripped, and is not able to vibrate at all at that point.

According to modern theory, a ray of light is propagated through space as vibrations in ether, which take place in all directions perpendicular to the line of propagation of the ray (Fig. 38A). If the ray be passed through a Nicol prism, cut in a certain manner from a crystal of Iceland spar (see a text-book of Physics), the vibrations get restricted and take place only in one direction. We say that the light has been *polarized*. In Fig. 38A, a beam, L , of ordinary light is shown to be passing in a direction perpendicular to the plane of the paper, the vibrations in ether taking place in all the directions, aa , bb , cc , etc. Fig. 38B shows a beam, L' , of polarized light, in which the vibrations take place only in one direction, *viz.*, aa . A plane drawn through the direction of the polarized ray, and perpendicular to the direction in which the ether vibrations occur, is called the

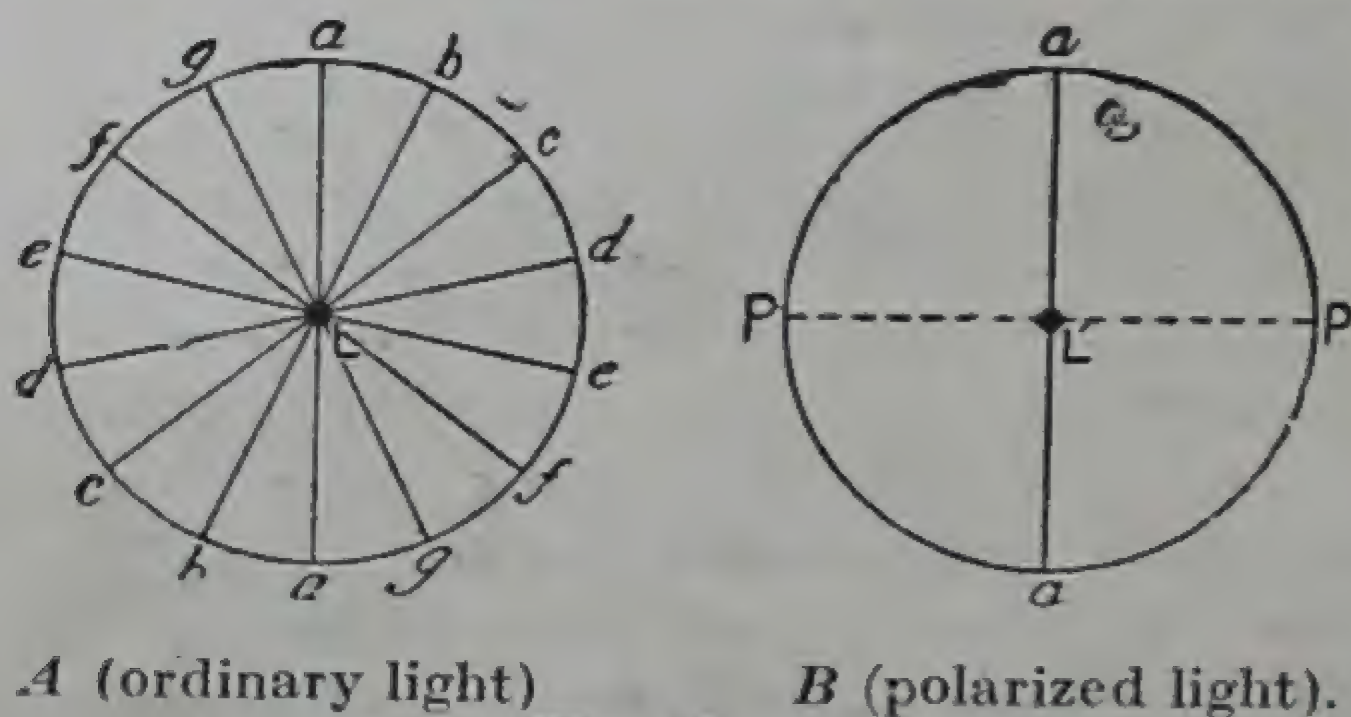


Fig. 38.

plane of polarization. In Fig. 38*B* the plane of polarization cuts the plane of the paper along the line *PP*.

If the polarized ray be passed through a second Nicol prism placed with its plane of polarization parallel to that of the first, the ray will pass through it as it did through the first one. If we rotate the second prism, the quantity of light passing through will continuously diminish until when the prism has been rotated through an angle of 90° , the light will be entirely cut off. In other words, the position of *maximum brightness* is followed at an interval of 90° by a position of *maximum darkness*, at an interval of 180° by a second position of maximum brightness, and at an interval of 270° by a second position of maximum darkness. The first Nicol prism, which causes polarization of light, is called the **polarizer**, while the second one, through which the polarized light is examined, is called the **analyser**.

48. Optical Activity. If, when the polarizer and the analyser are in the position of maximum darkness, we place between them a tube containing a solution of cane-sugar, the field of view will be found to have become more or less bright, showing that the plane of polarization of light falling on the analyser has been rotated by the cane-sugar solution. If now we slowly rotate the analyser towards the right, *i.e.*, clockwise, the position of maximum darkness will once again be reached. The angle through which the analyser has to be turned, in order to attain the position of maximum darkness once again, measures the degree of rotation of the plane of polarization by the cane-sugar solution.

Cane-sugar and other substances that have the power to rotate the plane of polarization in the above manner are said to be **optically active**. If, as in the case of cane-sugar, the analyser is to be turned towards the right (*i.e.*, clockwise) to re-attain the position of minimum brightness, the substance is said to be **dextrorotatory**; if, on the other hand, it is to be turned towards the left (anti-clockwise) the substance is called **levorotatory**.

49. Polarimeter. The simple arrangement of two Nicol prisms described above does not give accurate results, as the analyser, when arranged in the position of maximum darkness, can be turned through a small angle in either direction without allowing any light to pass through. Various types of polarimeters have been designed to overcome this difficulty. One of those in common use is the Laurent half-shadow polarimeter shown in Fig. 39.

The arrangement of the optical parts of this instrument is shown in Fig. 40. Monochromatic light from a sodium lamp, *S*, is passed through a cell, *C*, containing 6 per cent. potassium dichromate solution, which serves to absorb the blue or violet rays. Next it

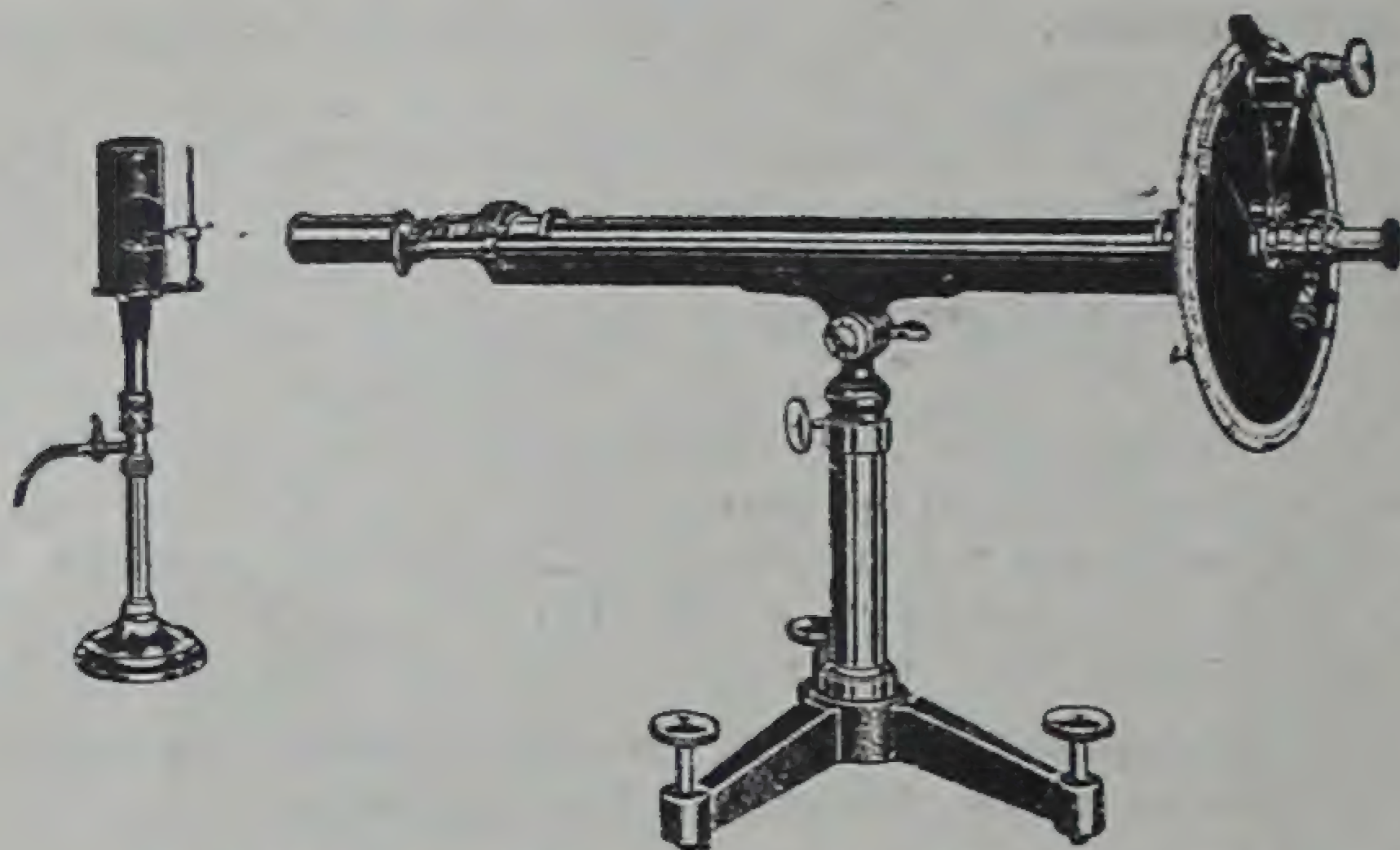


Fig. 39. Laurent's Half-shadow Polarimeter.

passes through the collimating lens, *L*, which serves to render the rays parallel, and then through the polarizer, *P*. The polarized light passes through the half-shade, *H* (see below), and then through the

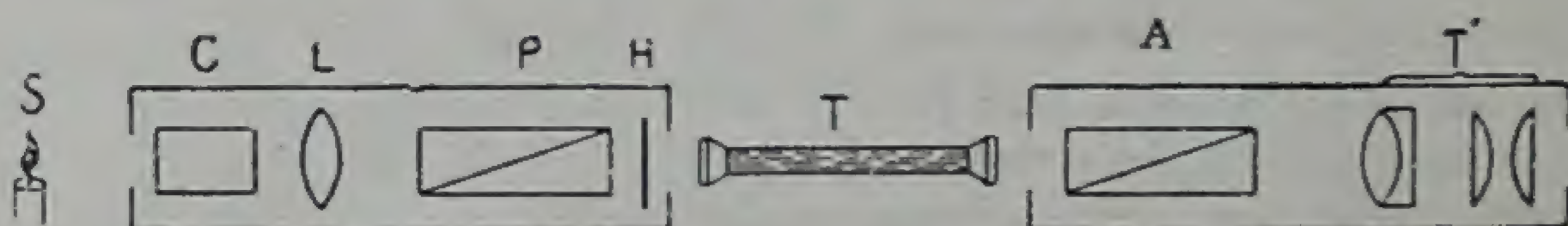


Fig. 40. Optical Parts of the Half-shadow Polarimeter.

liquid under examination contained in the observation tube, *T*. After traversing the liquid, the polarized light passes through the analyser, *A*, and finally emerges from the instrument through the eyepiece of the telescope, *T'*. The analyser may be rotated through any desired angle, and the amount of rotation measured on a graduated scale.

The half-shade, *H*, serves to determine exactly the point of maximum darkness. It consists of a combination of semi-circular plates of glass and quartz. Over a certain range of the scale the right-hand half of the field is darker than the left; beyond this range, the left-hand half gets darker than the right-hand half. The intermediate position where the illumination is uniform on the two sides of the field is taken as the zero point.

Expt. 19. Prepare a 50 per cent. solution of *pure* glucose. (If the solution is not quite clear, it may be clarified by adding a little basic lead acetate solution and filtering through a fluted filter.) Carefully clean an observation tube and the two circular glass discs used to cover the two ends of the tube. Set up the polarimeter in a dark room, and, using an observation-tube filled with water, determine the zero point of the polarimeter. Then replace the observation tube containing water with the one filled with sugar solution, and read the angle of rotation.

50. Specific Rotation. The angle of rotation produced by an optically active substance is directly proportional to the length of the liquid column traversed by the polarized light, and, in the case of a solution, to its concentration. It is also dependent on the temperature and on the wave-length of the light used; hence in all polarimetric observations we use the monochromatic light provided by the sodium flame (the D line).

The optical activity of a substance is represented by its *specific rotation*, $[\alpha]$, the value of which, in the case of a liquid, is given by the expression.

$$[\alpha]_D^t = \frac{a}{l \times d}$$

where a is the observed angle of rotation, t the temperature in degrees centigrade, l the length in decimetres of the liquid column in the observation tube, and d the density of the optically active liquid at the temperature of the experiment. The fact that sodium light has been used in the experiment is indicated by the letter D .

In the case of a solution of an optically active substance in water, or some other optically inactive solvent, the above expression becomes

$$[\alpha]_D^t = \frac{a}{l} \times \frac{v}{w}$$

where w is the weight of the substance in grams present in v c.c. of the solution.

The specific rotations at 20° of a few optically active substances are given in the following table:—

SUBSTANCE	$[\alpha]_D^{20^\circ}$
Cane sugar	+66.5°
Glucose	+52.5°
Fructose	-92°

For comparing the optical activities of different substances we employ the term **molecular rotation**. This is denoted by $[M]$ and is obtained by multiplying the specific rotation of a substance by its molecular weight and dividing by 100 in order to avoid unwieldy figures:

$$[M] = \frac{[\alpha]M}{100}$$

51. Saccharimetry. In technical practice, the strength of a solution of cane-sugar is determined by means of a special form of polarimeter, known as a **saccharimeter** (See Fig. 41). In this instrument the scale expressing angular rotation is replaced by one graduated according to a system indicating percentages. The polarizer and the analyser are stationary, and the rotation of the solution is read by moving a quartz wedge between the solution and the analyser, until, at a certain thickness, the rotation of the wedge neutralizes or “compensates” the rotation of the solution. The quartz wedge is, therefore, termed a **compensator**. The scale reading percentages is attached to the compensator. The 100° point of the scale corresponds to the rotation of a definite weight (26 grams) of pure dry sucrose present in 100 c.c. of aqueous solution and measured in a 2 dm. tube. An electric lamp is usually employed

as a source of light, for which use the saccharimeter is provided with a standard dichromate filter, or coloured glass of equivalent spectral value.

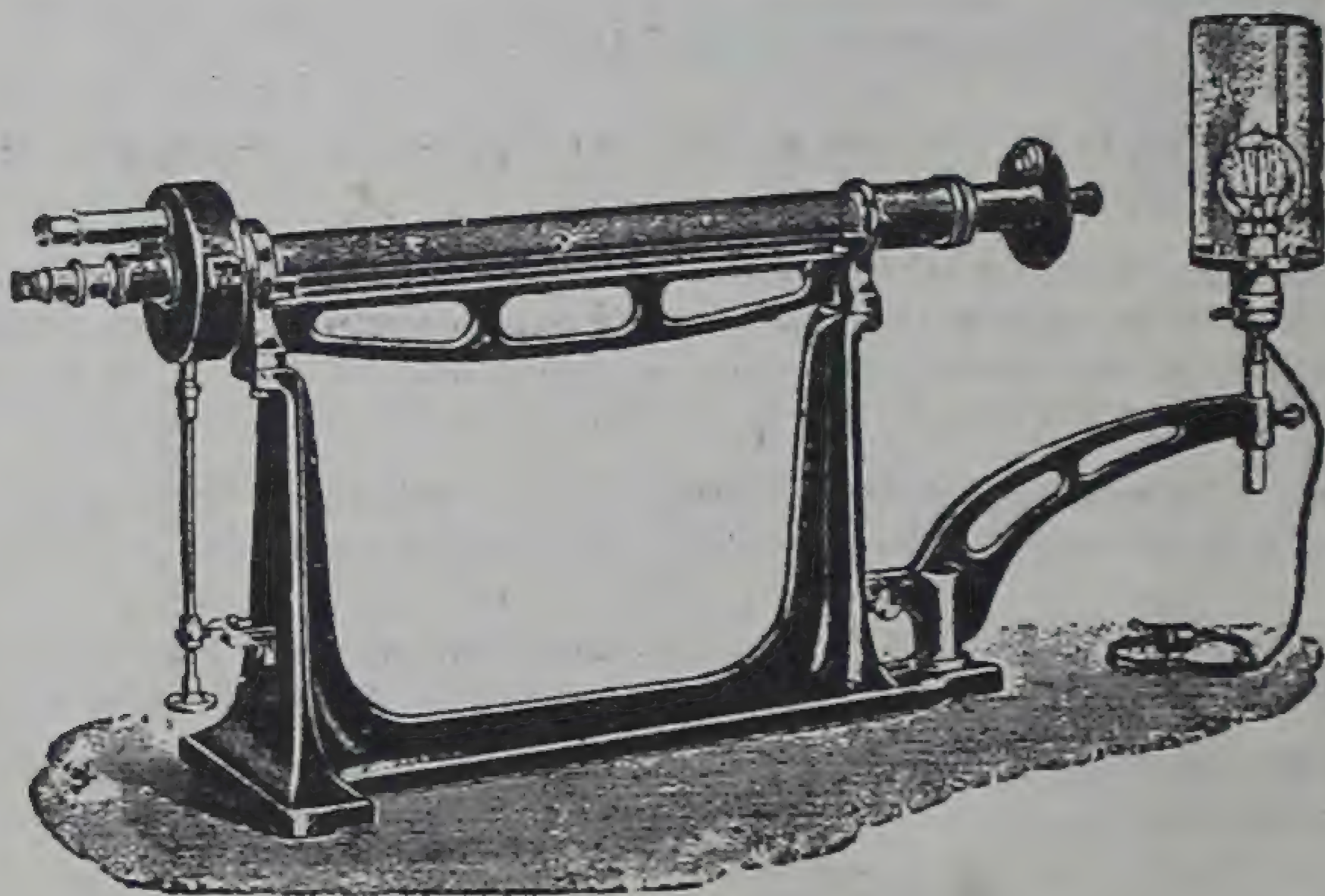


Fig. 41. Saccharimeter.

QUESTIONS

1. Explain the following terms: (a) *polarized light*. (b) *optical activity*, (c) *specific rotation*, and (d) *molecular rotation*.
2. Describe with a neat diagram the various optical parts of a polarimeter.
3. How is the [concentration of a solution of cane-sugar determined in technical practice? Describe carefully the various optical parts of a saccharimeter. In what important respects does it differ from a polarimeter?

CHAPTER VIII

STEREOCHEMISTRY

52. Discoveries of Biot, Haüy and Herschel. In 1813, Biot showed that thin plates of quartz, cut at right angles to the main axis, turned the plane of polarization of light through angles proportional to the thickness of the plates. He also noticed that while some quartz crystals gave plates having a dextro-effect on the polarized light, others yielded plates having a levo-effect. In 1815, he made the further important observation that certain organic substances, e.g., turpentine oil and solutions of cane-sugar and tartaric acid, also possessed the power of turning the plane of polarization of light. Since then, many more optically active inorganic substances, e.g., sodium chlorate, sodium bromate⁹¹ and ammonium lithium sulphate, and a far greater number of optically active organic substances have been discovered.

Biot found that a fundamental difference existed between optically active inorganic and organic substances. The former exhibit this activity only in the crystalline form, while the latter show it in the liquid and even in the gaseous state. Thus, if the crystalline forms of quartz or sodium chlorate be destroyed by fusion or solution, the optical activity at once disappears. This is not so in the case of cane-sugar or tartaric acid; solutions of these substances are optically active. Hence, Biot concluded that in quartz, etc., the optical activity is due to the *arrangement* of the crystalline particles, while in tartaric acid, etc., it is due to the *constitution* of the molecules.

The famous crystallographer Haüy had shown that the fully developed "hemihedral" quartz crystals existed in two closely related forms having certain characteristic facets, or faces, which in the case of one form lay to the right and in the other to the left, the two kinds of crystals being related as an object to its image, or as a right hand to a left hand. In the terminology, of crystallography, they are said to be *enantiomorphous* (Gk. *enantios*, opposite; *morphe* form).

In 1820, Herschel correlated the observations of Haüy and Biot, and showed that plates cut from quartz crystals having right-handed hemihedral facets turned the plane of polarization to the

right and those having left-handed hemihedral facets turned it towards the left. Thus a useful relation between hemihedrism and optical rotation of crystalline substances was discovered.

LOUIS PASTEUR
(1822—1895)

Pasteur, the well-known French scientist, rendered a signal service to chemistry when he set himself to the study of tartaric acids which resulted in the establishment of *Stereochemistry*. His other important contribution is his famous work on the phenomenon of Fermentation. Pasteur's devotion to his work is shown by the interesting fact on record that he actually forgot his own wedding day and had to be hurriedly fetched from his laboratory by one of his friends.

Pasteur's well-known humanitarian work on hydrophobia won for him an everlasting honour. The Pasteur Institute in Paris and other similar institutes all over the world bear testimony to this.



53. Pasteur's Work on Tartaric Acids. Tartaric acid obtained from grape-juice is optically active and turns the plane of polarization of light to the right. The mother liquor obtained in the purification of this acid contains another acid called *racemic acid*, which, since it possesses exactly the same *chemical* properties as tartaric acid, must have the same structure as the latter. However, racemic acid differs from tartaric acid in its *physical* properties, and is optically inactive.

In 1844, Mitscherlich published the results of his crystallo-graphic examination of the sodium-ammonium salts of tartaric and racemic acids. He stated that these double salts "have the same chemical composition, the same crystalline form with the same angles...but the dissolved tartrate deviates the plane of polarization, while the racemate is indifferent."

"This note of Mitscherlich's," says Pasteur, "attracted my attention forcibly at the time of its publication. I was then a pupil in the *Ecole Normale*, reflecting in my leisure moments on these elegant investigations of the molecular constitution of substances, and having reached—as I thought at least—a thorough comprehension of the principles generally accepted by physicists and chemists, the above note disturbed all my ideas. What precision in every detail! Did two substances exist which had been more fully studied and more carefully compared as regards their properties? But how, in the existing condition of the science, could one conceive of two substances so closely alike without being identical?"

Pasteur had once wondered whether the organic substances possessing optical activity in solution would show hemihedrism in their crystals. He had found that tartaric acid, which is optically active, *did* form hemihedral crystals, while racemic acid, which is optically inactive, did *not* show this phenomenon. "Hence," says Pasteur, "I thought at once that Mitscherlich was mistaken on one point. He had not observed that his sodiumammonium tartrate was hemihedral while his racemate was not. If this is so, the results in his note are no longer extraordinary; and further, I should have, in this, the best test of my preconceived idea as to the inter-relation of hemihedry and the rotatory phenomena."

In 1846, Pasteur proceeded to re-investigate the problem. The result of his research may be stated in his own words:—

"I hastened, therefore, to re-investigate the crystalline form of Mitscherlich's two salts. I found, as a matter of fact, that the tartrate was hemihedral, like all the other tartrates which I had previously studied, but, strange to say, the racemate was hemihedral

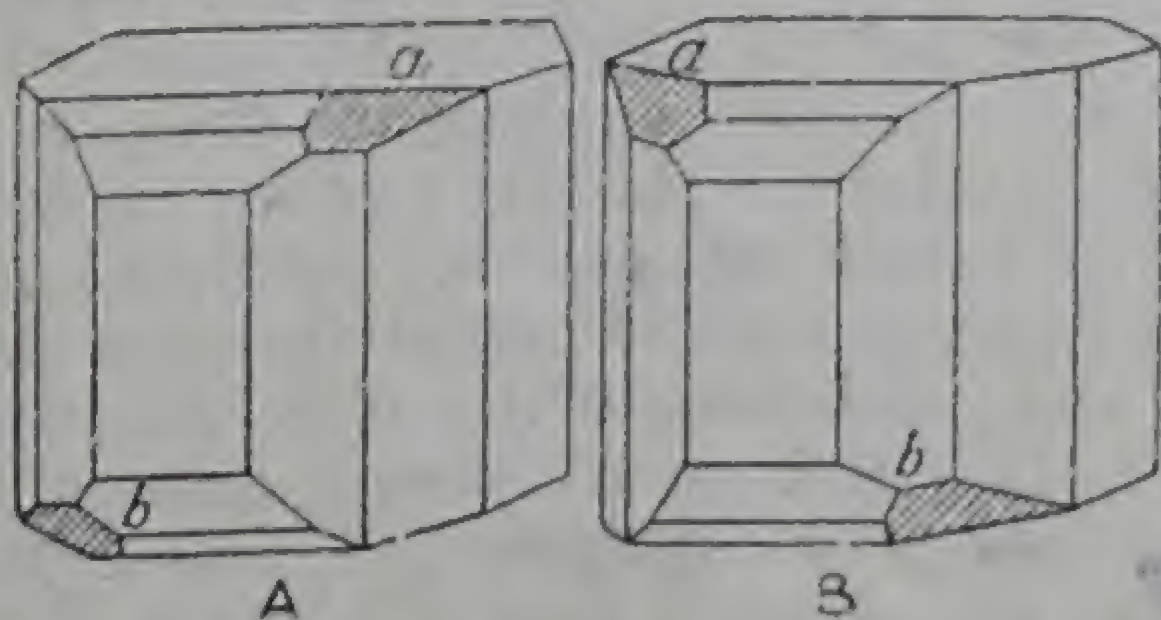


Fig. 42. Crystals of (A) Sodium Ammonium *d*-Tartrate, (B) Sodium ammonium *l*-Tartrate.

also. Only, the hemihedral faces, which in the tartrate were all turned the same way, were, in the racemate, inclined sometimes to the right and sometimes to the left (Fig. 42 *A* and *B*). In spite of

the unexpected character of this result, I continued to follow up my idea. I carefully separated the crystals which were hemihedral to the right from those hemihedral to the left, and examined their solutions separately in the polarizing apparatus. I then saw with no less surprise than pleasure that the crystals hemihedral to the right deviated the plane of polarization to the right, and that those hemihedral to the left deviated it to the left, and when I took an equal weight of each of the two kinds of crystals, the mixed solution was indifferent towards the light in consequence of the neutralization of the two equal and opposite individual deviations."

Pasteur's announcement of the above discovery was received at first with incredulity by the scientific world, and the French Academy of Sciences delegated Biot, the greatest living authority on polarized light, to examine Pasteur's statements. An account of the dramatic scene which followed has been left on record by Pasteur himself:—

"He [Mr. Biot] sent for me to repeat before his eyes the several experiments. He gave me racemic acid which he had himself previously examined and found to be quite inactive to polarized light. I prepared from it in his presence the sodium ammonium double salt, for which also he desired himself to provide the soda and ammonia. The liquid was set aside for slow evaporation in one of the rooms of his own laboratory, and when 30 to 40 grams of crystals had separated he again summoned me to the College de France, so that I might collect the dextro- and levo-rotatory crystals before his eyes, and separate them according to their crystallographic character, asking me to repeat the statement that the crystals which I should place on his right hand would cause deviation to the right, and the others to the left. This done, he said that he himself would do the rest. He prepared the carefully weighed solutions, and at the moment when he was about to examine them in the polarimeter, he again called me into his laboratory. He first put the more interesting solution, which was to cause rotation to the left, into the apparatus. Without making a reading, but already at the first sight of the colour tints presented by the two halves of the field in the Soleil saccharimeter, he recognized that there was a strong levo-rotation. Then the illustrious old man, who was visibly moved, seized me by the hand, and exclaimed: 'My dear child, I have so loved the sciences throughout my life that this makes my heart leap with joy!'"

Pasteur further discovered that of the two kinds of crystals obtained from sodium ammonium racemate, the one showing dextro-rotation gave an acid identical with natural tartaric acid in every respect, whereas the other gave an acid which in aqueous solution

showed levo-rotation. On mixing concentrated solutions of equal amounts of the *d*- and *l*- tartaric acids, obtained as above, a precipitate of optically inactive racemic acid was at once formed. Thus Pasteur was able to show both analytically, and synthetically, that racemic acid is a mixture of equal quantities of tartaric acid obtained from grapes and the hitherto unknown *l*-tartaric acid. For this reason racemic acid is also called *dl*-tartaric acid.

Pasteur found that *d*- and *l*-tartaric acids were identical in crystalline forms, melting-point and solubility. The only two points in which they differ from each other are: (*a*) their rotatory powers, which are equal but opposite, and (*b*) the disposition of the hemihedral facets of their crystals, which are related to one another as an object and its image. Pairs of chemically identical substances related in this manner are called optical isomers, optical antipodes, enantiomers or enantiomorphs.

At the time of Pasteur's researches, the theory of molecular structure of Kekulé (Sec. 30) had not yet been pronounced. It was, therefore, not possible to represent structurally the *d*- and *l*- tartaric acids. However, Pasteur's keen judgment led him to conclude that the molecules of the two tartaric acids possessed identical composition and structure, but differed in spatial arrangement so that one was the mirror image of the other.

54. Wislicenus' View on Isomerism of Lactic Acids.

In 1863, Wislicenus published a remarkable memoir on the synthesis of lactic acid. His method consisted in acting upon ethylene chlorohydrin with potassium cyanide and hydrolysing the nitrile so formed. In 1780, Scheele had discovered lactic acid in sour milk, and, in 1807, Berzelius obtained a similar acid, called *sarc*olactic acid from muscle juice. The acid was found to differ from the sour-milk acid in being dextro-rotatory, the former being optically inactive. Chemically, the two acids were found to be identical, though they differed in certain physical properties. (See table under Lactic Acid). Wislicenus meditated upon this remarkable fact for several years, and in 1873, expressed the following view: "If it is once granted that molecules can be structurally identical and yet possess dissimilar properties, it can only be explained on the ground that the difference is due to a different arrangement of their atoms in space."

55. Le Bel and van't Hoffs' Theory. Stimulated by the work of Pasteur and of Wislicenus, a "space theory" of the isomerism of optically active compounds was developed independently and almost simultaneously in 1874 by Le Bel and van't Hoff. According to this theory *the four valencies of a carbon atom are directed towards*

the four corners of a regular tetrahedron, constructed around the carbon atom as centre.

By reference to Fig. 43 it can be readily seen that if the four solid angles of the tetrahedron are occupied by four *different* atoms or groups (*a*, *b*, *c* and *d*), the resulting configuration is capable of existing in a right-handed form and a left-handed form. The mirror-image relationship of the molecule is repeated in the optical and crystallographic properties of the substances. The stereo-chemical figures such as those given in Fig. 43 are called *space formulæ*. By reference to these it

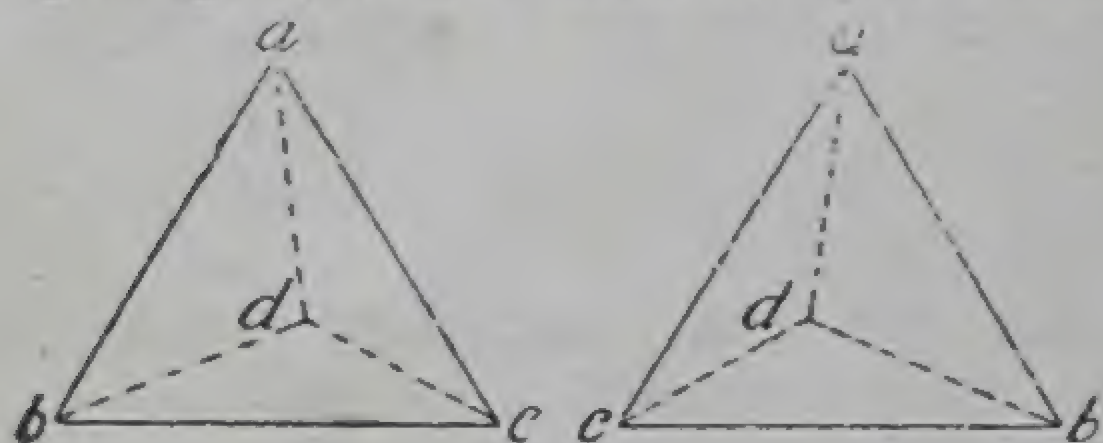


Fig. 43.

will be seen that *the molecule of an optically active compound possesses no plane of symmetry.*



JACOBUS HENRICUS VAN'T HOFF (1852-1911)

was a Dutch physical chemist, born in Rotterdam, Holland. He began his career of research with experiments regarding cyanoacetic and malonic acids. In 1874, he put forward the "theory of asymmetric carbon atom," which laid the foundation of Stereochemistry. In 1884, he published his very important work on the application of thermodynamics to chemical reactions, which is usually regarded as his greatest contribution to physical chemistry. In 1886, he published the results of his study of dilute solutions, and showed the analogy existing between them and gases.

A carbon atom linked to four different atoms or groups is known as an *asymmetric carbon atom*. Of course it is not the atom itself that

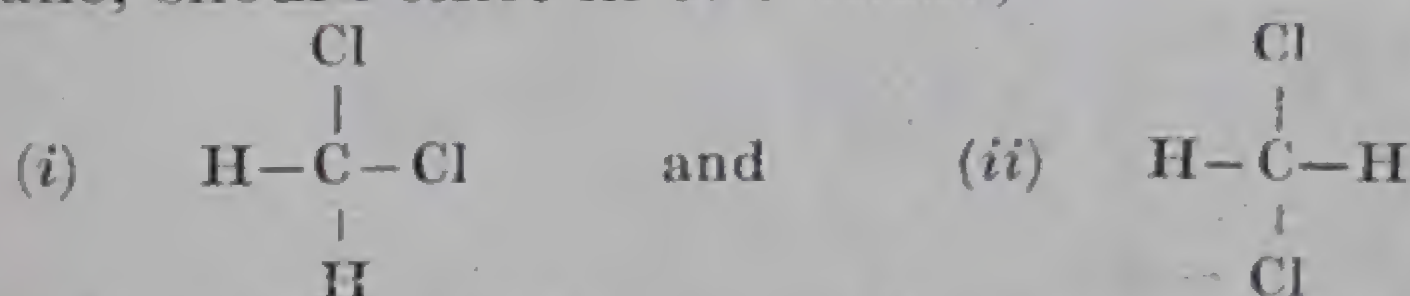
is asymmetric, but the molecule that contains it. The stereo-isomerism exhibited by compounds containing one or more asymmetric carbon atoms is called **optical isomerism**, since it is associated with optical activity, and is to be distinguished from *geometrical isomerism* (Sec. 62), which is not necessarily associated with optical activity.

Le Bel and van't Hoff's theory of stereoisomerism is supported by the following facts:—

(1) All substances capable of existing in optically active forms possess one or more asymmetric carbon atoms.

(2) If by any means the asymmetric character of the molecule is destroyed, [e.g., in the case of lactic acid, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{COOH}$, by reduction to propionic acid, $\text{CH}_3\cdot\text{CH}_2\text{COOH}$], the optical activity also disappears.

(3) The absence of isomeric forms of such substances as methylene chloride, CH_2Cl_2 , which, if all the four carbon valencies lay in the same plane, should exist in two forms,



In spite of much research, no such isomerism has ever been found to exist.

(4) Bragg's X-ray analysis of the structure of diamond shows that in this substance the carbon atoms are united by tetrahedrally directed valency bonds (Fig. 44).

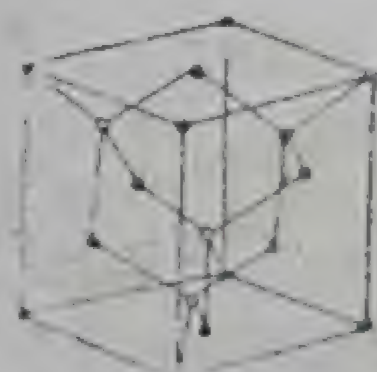
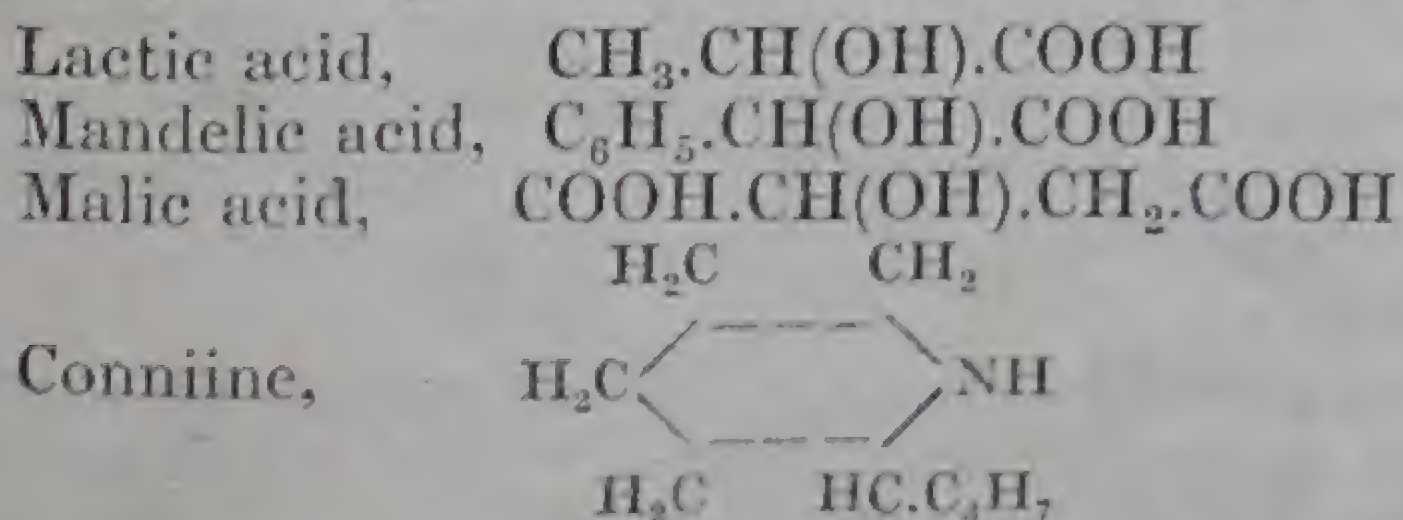


Fig. 44. The Diamond Lattice.

56. Isomerism of Compounds containing One Asymmetric Carbon Atom. The more familiar examples of compounds containing one asymmetric carbon atom are:



Each of these compounds can exist in three forms, two of which are optically active and the third optically inactive. Of the two optically active forms, one is dextro-rotatory and the other levorotatory. These two forms turn the plane of polarization through the *same* angle, though in *opposite* directions. With the exception of this point, the two isomerides possess exactly identical properties. The third form is produced by mixing equimolecular quantities of the *d*- and *l*-forms and

is optically inactive, owing to the mutual, or, as we say, **external compensation** of the two constituents. An inactive product of this type is called a **racemic compound** or *racemic mixture* and is distinguished by the prefix *r-* or *dl-*. When in the crystalline state, *dl*-form is frequently a definite compound having double the molecular weight of the *d-* or *l*-modification. In solution, or in the liquid state, a racemic compound exists as a mixture of the *r*-modification in equilibrium with equivalent quantities of the *d*- and *l*-forms. A racemic compound may be resolved into its optically active components by methods described in Sec. 61.

57. Compounds containing Two Asymmetric Carbon Atoms. A compound containing two *dissimilar* asymmetric carbon atoms, is capable of existing in 2^2 , or 4, optically active forms, made up of two pairs having equal and opposite rotatory power; in addition to these there exist two inactive racemic forms. Representing the two carbon atoms by *A* and *B* and their different spatial configurations by signs + and −, the four optically active forms are:

(1)	(2)	(3)	(4)
+A	−A	+A	−A
+B	−B	−B	+B

An example of this class is $\text{C}_6\text{H}_5\text{CHBr.CHBr.COOH}$, dibromocinnamic acid, which exists in six forms, four active and two racemic.

Compounds containing two structurally *similar* asymmetric carbon atoms can have three configurations. In this case $A=B$, and hence the configurations (3) and (4) of the preceding case become identical:

(1)	(2)	(3)
+A	−A	+A
+A	−A	−A

Modifications (1) and (2) are optically active, while (3) is inactive by, what is termed, **internal compensation**, the dextro-rotatory effect of one of the carbon atoms being exactly counterbalanced by the levorotatory effect of the other. A compound of this type is described as *i-* or *meso*-compound, and, unlike a racemic compound, is non-resolvable.

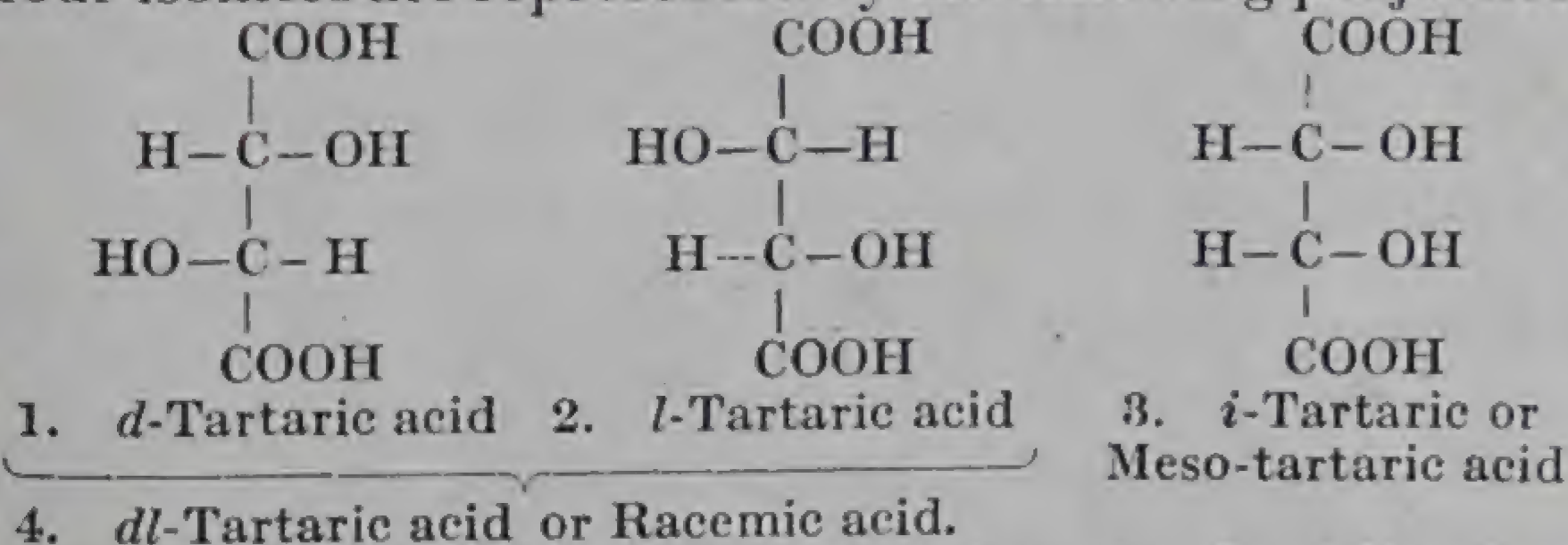
In addition to the above three forms, there exists an inactive racemic form containing equivalent quantities of the active enantiomorphs, the inactivity being due to *external* compensation.

The best known example of isomerism exhibited by compounds containing two structurally similar asymmetric carbon atoms is furnished by dihydroxysuccinic acid, or **tartaric acid**, which exists in four forms. As already mentioned the acid derived from grape-juice is *d*-tartaric acid. The optically inactive **racemic acid** obtained from the mother liquor of *d*-tartaric acid, is the *dl*-acid formed by the union of equivalent quantities of *d*- and *l*-tartaric acids. It can be

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resolved into its *d*- and *l*- constituents by the mechanical separation of the hemihedral crystals of its sodium ammonium salt, followed by treatment of the two kinds of crystals with a mineral acid. The internally compensated form, known as mesotartaric acid, is readily obtained (along with *dl*-tartaric acid) by heating *d*-tartaric acid with a little water at 165°.

The four isomers are represented by the following projection formulæ¹:



The properties of the four acids are given in the following table:—

Property	<i>d</i> -Tartaric acid	<i>l</i> -Tartaric acid	<i>i</i> -Tartaric acid	Racemic acid
1. Crystals.	Monoclinic, anhydrous prisms; m.p. 170°; show hemihedral facets.	Same as the <i>d</i> -acid, except that the hemihedral facets are turned in opposite direction to those in <i>d</i> -acid.	Rectangular efflorescent plates; contain 1H ₂ O; m.p. 143°; show no hemihedral facets.	Rhombic, efflorescent crystals; contain 1H ₂ O; m.p. 206°; show no hemihedral facets.
2. Action on polarized light.	Dextro-rotatory.	Levo-rotatory.	Inactive by internal compensation.	Inactive by external compensation.
3. Sodium ammonium salt.	Crystals show hemihedral facets.	Crystals show hemihedral facets turned in the opposite direction to those in the <i>d</i> -tartrate.	Crystals show no hemihedral facets.	Two kinds of crystals, some hemihedral to the right, others to the left: mechanically separable.
4. Potassium hydrogen salt.	Sparingly soluble in water.	Sparingly soluble in water.	Readily soluble in water.	Readily soluble in water.

¹ The projection formula of an internally compensated stereoisomeride is identical with its mirror image; hence it can be made to coincide with the latter by rotation in the plane of the paper. If the projection formula of a stereoisomerides is not identical with its mirror image, i.e., if it cannot be made to coincide with the latter by rotation in the plane of the paper, it evidently represents an optically active stereoisomeride, the mirror-image representing the projection formula of the optical antipode.

58. Compounds containing more than two Asymmetric Carbon Atoms. The number of possible stereoisomerides increases rapidly with an increase in the number of asymmetric carbon atoms. A compound containing n asymmetric carbon atoms, each of which is structurally *different* from all the rest, can exist in 2^n stereoisomeric forms consisting of a number of pairs of mirror image isomerides having equal and opposite rotations. If two or more of the carbon atoms be structurally identical, some of the possibilities of isomerism will vanish as in the case of tartaric acids.

59. Physiological Distinction between Optical Antipodes. In their physiological action the optical isomers show a profound difference. Thus, *l*-nicotine, which is obtained from tobacco leaves, when injected into the blood of an animal, produces pain, excitation, and finally death. The *d*-nicotine, on the other hand, which can be obtained synthetically, causes only a strong temporary shivering when similarly injected. Several other cases of antipodes showing profound difference in their physiological action are known.

Pasteur explained this difference in physiological action by assuming that the nerve and tissue components of our bodies are themselves asymmetric, and consequently react differently towards dextro- and the levo-isomerides. Similar differences of a biochemical nature have been observed in the behaviour of optical antipodes towards ferments, and are utilized in the separation of racemic compounds into their optically active components.

60. Racemization. As already mentioned, *d*-tartaric acid, when heated with water under pressure, yields racemic acid. If *l*-tartaric acid be similarly treated, we get the same result. Many other optically active substances pass into the externally compensated forms when submitted to the action of heat or chemical reagents. Such a process of inactivation is called "racemization."

Werner explains the phenomenon of racemization by imagining that each of the four groups attached to the asymmetric carbon atom is in oscillation within an independent orbit. Under the influence of a racemizing agent the amplitude of the oscillation is increased, with the result that a mutual invasion of the orbits occurs. This makes it possible for the *d*-form to pass into the *l*-form, and *vice versa*. A dynamic equilibrium between the two forms is thus established when equal numbers of the two kinds of molecules have been produced.

61. Preparation of Optical Antipodes. The methods of preparation of optically active substances may be divided into the following classes:—

(1) Resolution of Racemic Compounds. When a compound containing one or more asymmetric carbon atoms is synthesized from optically inactive materials, it is found that the product is always optically inactive, consisting of equimolecular quantities of the *d*- and *l*-isomers. The methods that are employed for the resolution of such racemic compounds were all discovered by Pasteur. They are:—

(a) *Spontaneous Separation*. When the two antipodes form well developed crystals showing hemihedral facets, as in the case of sodium ammonium *d*- and *l*-tartrates (Sec. 53), the separation can be readily effected by hand-picking. The method is known as the “spontaneous” separation of the antipodes, since under proper conditions the dextro-rotatory molecules congregate spontaneously into one kind of crystals, while the levo-rotatory molecules assemble together to form the other kind of crystals. Such a separation occurs only below the so-called *transition temperature*. Thus, in the case of sodium ammonium racemate the transition temperature is 27° . If the crystallization be effected above this temperature, holohedral symmetrical crystals of the salt separate out, containing equal numbers of the dextro- and the levo-rotatory molecules. This method has a very limited application, since the formation of mechanically separable crystals has been observed in very few cases. It was first used by Pasteur in 1848 to resolve racemic acid. In 1892, Purdie and Walker made use of this method for resolving *dl*-lactic acid by the crystallization of the zinc ammonium salt.

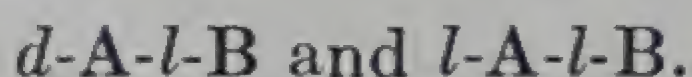
(b) *Biochemical Method*. This method is based on the fact that when bacteria, fungi, or yeasts are allowed to grow in a solution of a racemic compound, one of the optical antipodes is destroyed much faster than the other (selective¹ assimilation). Thus Pasteur, in 1851, discovered that when a species of the green mould, *penicillium glaucum*, is allowed to grow in a solution of ammonium racemate, the *d*-tartrate is completely destroyed, while the *l*-salt is left practically unaffected. In 1890, Fischer found that yeasts fermented optically inactive sugars, synthesized by him, such as *dl*-glucose and *dl*-fructose, destroying in each case the naturally occurring *d*-sugar and leaving behind the hitherto unknown *l*-sugar. The selective assimilation is

¹ It was formerly supposed that the action of a micro-organism was confined only to one of the antipodes, the other being left entirely unaffected. In 1903, McKenzie and Harden showed that this is not the case; but that *both* the enantiomorphs are attacked, though at very different rates. It has further been shown that an organism may be *acclimatized* to the second form, so as eventually to cause its rapid fermentation. Thus, a micro-organism which will normally bring about the fermentation of *d*-tartaric acid more readily than that of the *l*-acid, may, if starved, be eventually persuaded to attack the *l*-isomer and after a time it develops such a taste for the *l*-acid that it scarcely touches the *d*-isomer.

supposed to be due to the asymmetry and optical activity of the enzymes present in the micro-organism. According to Fischer, the molecular configuration of the enzyme concerned conforms to that of the isomer undergoing fermentation as the key to the lock.

This method, like the previous one, is of use only in a few cases. Moreover, it is slow and uneconomical, as at least half of the substance is destroyed.

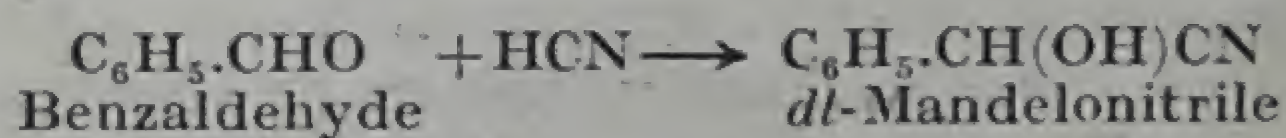
(c) *Salt formation with Active Bases or Acids.* This is the most important method, and is based on the following principle: When a racemic mixture of an optically active acid ($d\text{-A} + l\text{-A}$) is made to combine with an optically active (say levo-rotatory) base, $l\text{-B}$, two salts are produced, *viz.*,



The pair of salts (unlike that obtained with an optically inactive base, such as sodium or ammonium hydroxide) is *not* enantiomorphous. The two salts, therefore, possess different solubilities and may be readily separated by fractional crystallization. The individual salts may then be decomposed by hydrochloric acid to obtain the two optically active acids. For example, Pasteur, in 1853, found that racemic acid when combined with quinine, a levo-rotatory alkaloid, gives the far less soluble quinine d -tartrate and the fairly soluble quinine l -tartrate. With cinchonine, on the other hand, l -tartrate is found to be the less soluble salt; hence, on fractional crystallization, this salt separates out first.

Similarly, a racemic base may be separated into its optically active constituents by making it combine with an optically active acid, and submitting the resulting salts to fractional crystallization.

(2) *Asymmetric Synthesis.* As is well known, when a compound containing an asymmetric carbon atom is synthesized from substances having no asymmetric carbon atoms, the new product is always of the racemic type, *e.g.*,

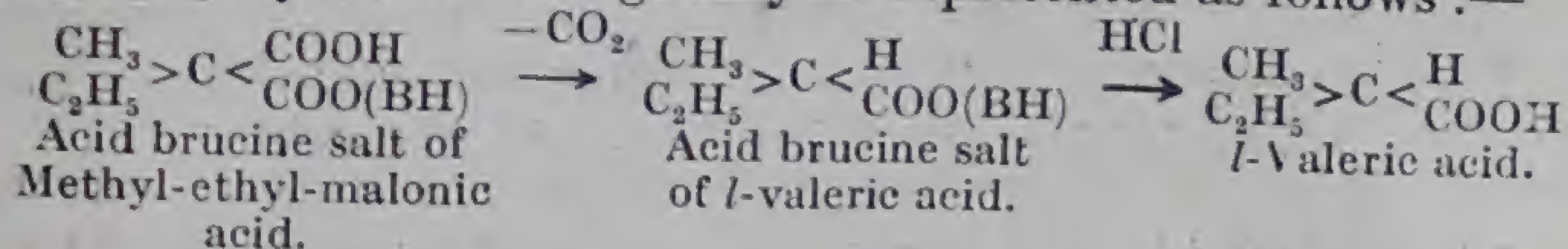


On the other hand, if a compound containing an asymmetric carbon atom be synthesized under the influence of an *optically active grouping* which is subsequently removed, the product may exhibit optical activity. A synthesis of this type is called *asymmetric synthesis*.

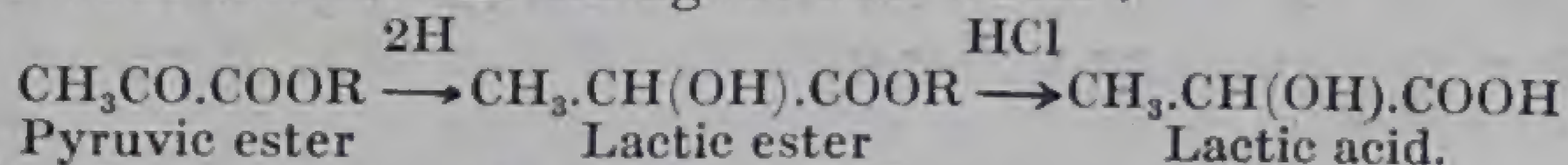
Of the many asymmetric syntheses effected by various investigators the following may be mentioned:—

(i) Marckwald, in 1904, prepared an active l -valeric acid by heating at 170° the acid brucine salt of methyl-ethyl-malonic acid, until no more carbon dioxide was evolved. Representing the brucine molecule,

$C_{23}H_{26}N_2O_4$, by B, the change may be represented as follows :—

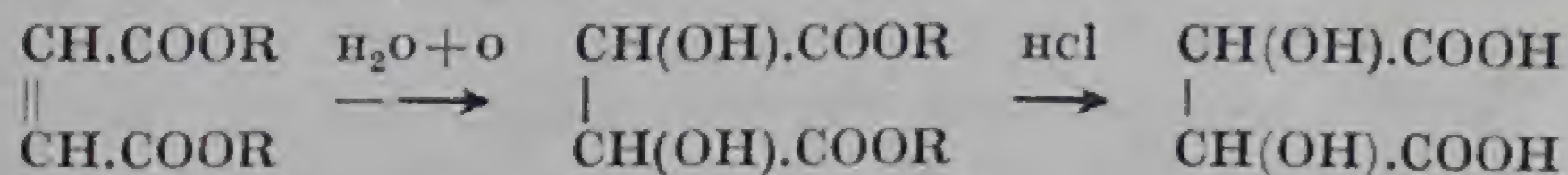


(ii) Another example of asymmetric synthesis is the preparation of lactic acid, containing an excess of the *l*-isomer, by McKenzie and his co-workers. This was effected by reducing *l*-menthyl (or *l*-bornyl) pyruvate with aluminium amalgam and water :



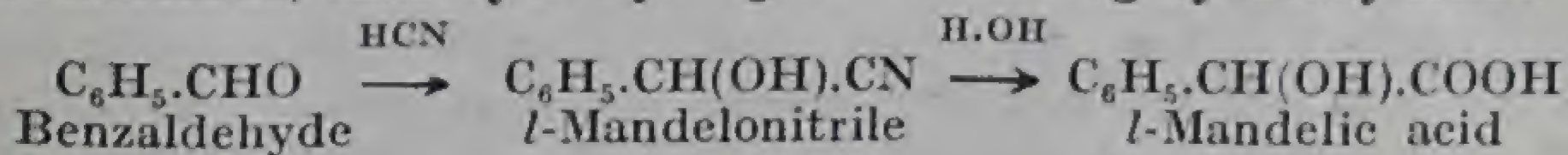
When the *d*-amyl ester of pyruvic acid was used, an excess of the *d*-lactic acid was formed.

(iii) McKenzie and Wren found that when *l*-bornyl ester of fumaric acid is oxidized by means of potassium permanganate, a mixture of *d*- and *l*-tartaric ester, containing an excess of the latter, is formed. When the bornyl group is removed by treatment with hydrochloric acid, the levo-rotatory tartaric acid is obtained.



When *d*-bornyl fumarate is used, the product is found to contain an excess of *d*-tartaric ester.

(iv) Rosenthaler, in 1909, obtained *l*-mandelic acid by making benzaldehyde combine with hydrogen cyanide in the presence of the enzyme emulsin, and hydrolysing the resulting cyanohydrin :

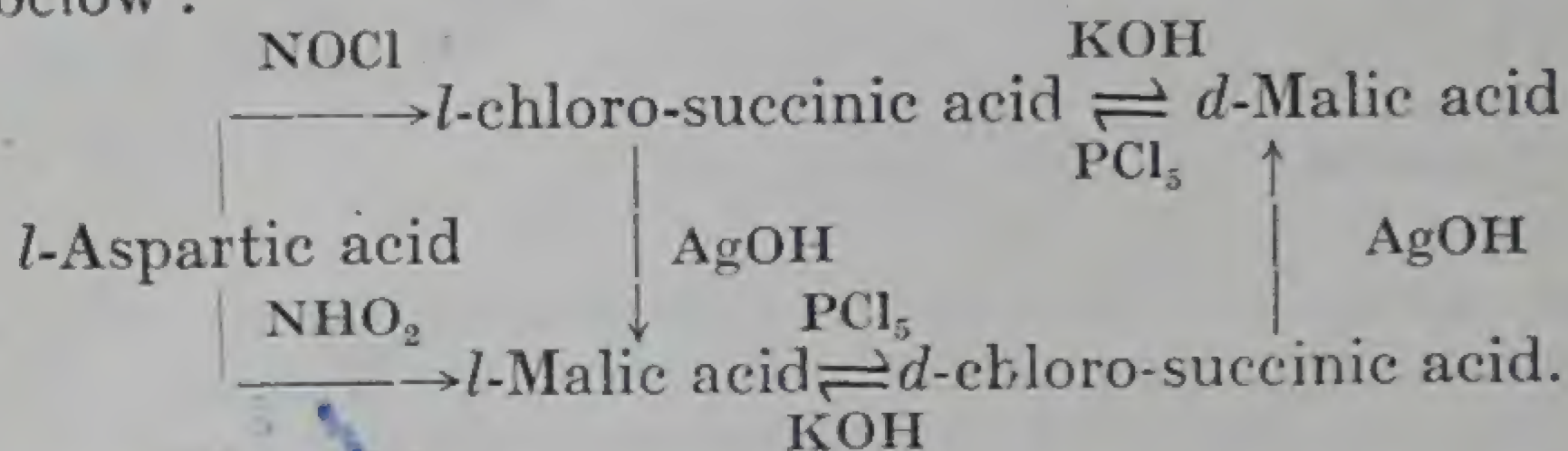


(3) Production of one Optical Antipode from Another. An optical isomer may be obtained from its antipode in two ways :

(a) The optical isomer available is first racemized (Sec. 60) and the second isomer is then separated from the racemic mixture (Sec. 61).

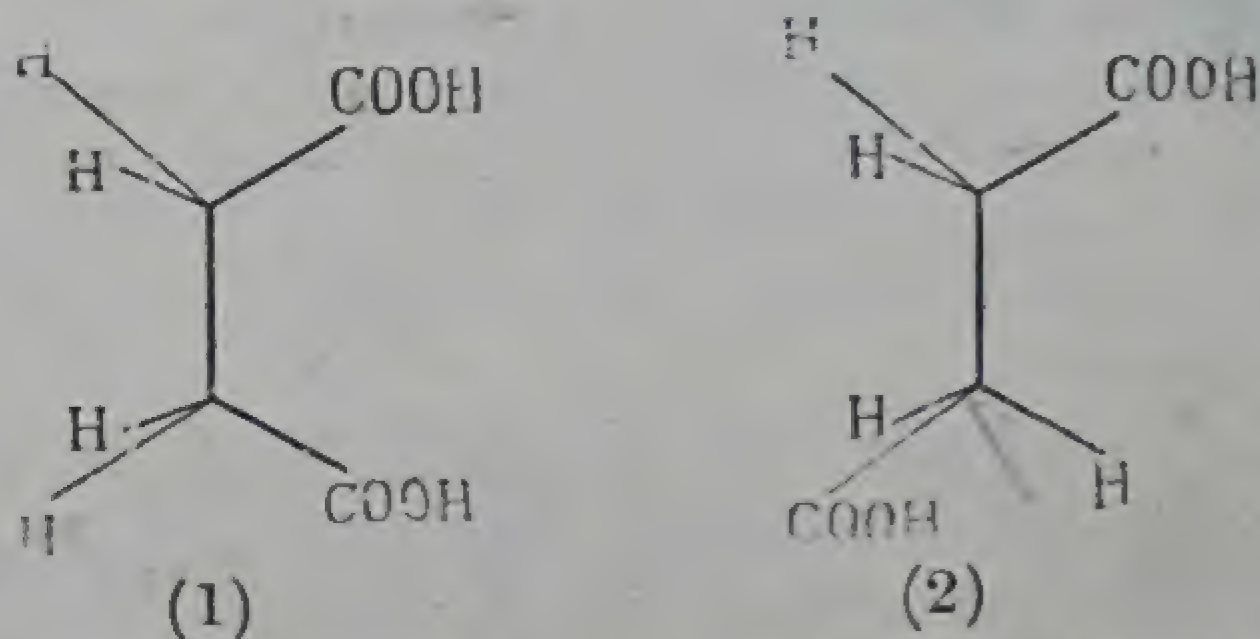
(b) *Optical Inversion* or *Walden Inversion*. Walden, in 1893, found that, when one radical in an optically active compound is replaced by another, the configuration of the new compound may be influenced by the nature of the reagent employed. Thus, when *l*-chlorosuccinic acid is treated with silver hydroxide *l*-malic acid is formed, but if dilute potassium hydroxide be used to bring about the hydrolysis, *d*-malic acid is obtained. A change of configuration effected in this manner by means of suitable reagents is called "optical inversion" or "Walden inversion."

A complete scheme summarizing the observations of Walden is given below :



Emil Fischer, in 1911, showed that α -amino and α -halogen acids undergo optical inversion under suitable treatment. Many other cases of Walden inversion have been studied,¹ but no comprehensive explanation of the phenomenon has so far been offered.

62. Geometrical Isomerism. Whereas tartaric acid exhibits stereoisomerism, succinic acid does not, and is known only in one form. If the single bond that unites the tetrahedra representing the two carbon atoms were of a rigid type, the following two configurations for succinic acid would be possible.

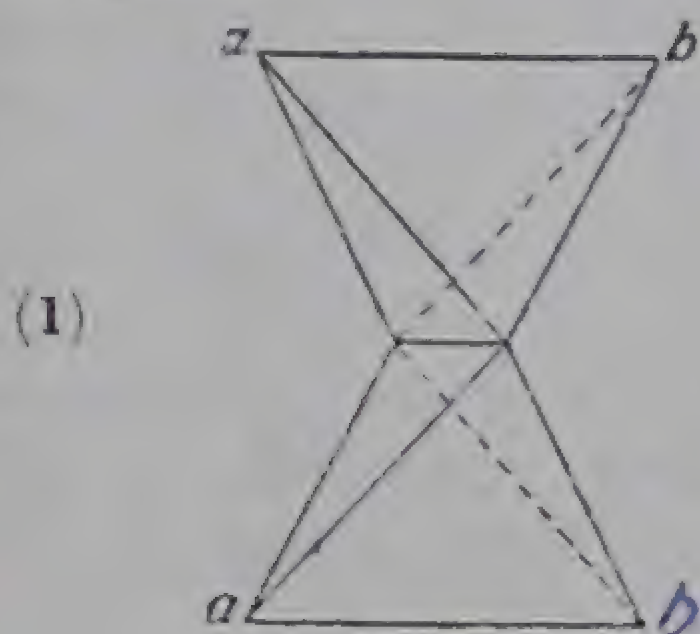


But, since the isomerism among symmetrical saturated substances of the above type is not known, it must be concluded that *there occurs a free rotation of carbon atoms about the single bond*. It is assumed that the atoms or groups united to the singly bound carbon atoms exert a mutual directive influence on each other, until by virtue of free rotation about the common axis, the whole system acquires the most stable configuration.

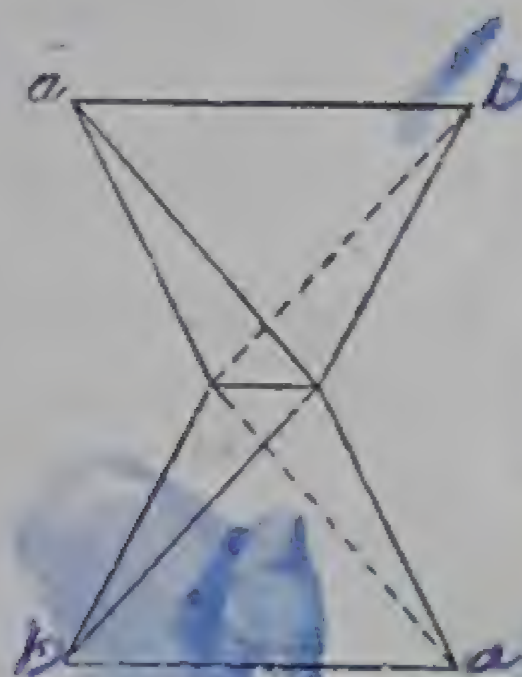
With compounds containing doubly bound carbon atoms, however, the case is otherwise. All independent rotation of the tetrahedra here ceases, as they are held together at *two* different points. Hence, compounds of the type $\begin{smallmatrix} a \\ b \end{smallmatrix} > \text{C} = \text{C} < \begin{smallmatrix} a \\ b \end{smallmatrix}$ and also of the type $\begin{smallmatrix} a \\ b \end{smallmatrix} > \text{C} = \text{C} < \begin{smallmatrix} c \\ d \end{smallmatrix}$ are found to exist in two stereoisomeric forms having the

¹ See Bawa Kartar Singh's paper : "The Walden Inversion," Journal of the Science Association, Maharajah's College, Vizianagaram, Vol. II, No. 1, pp. 1 to 11.

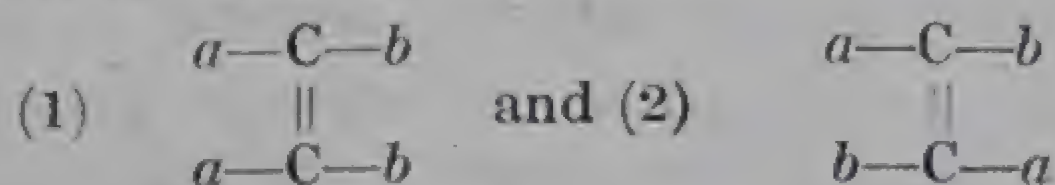
configurations :



and (2)

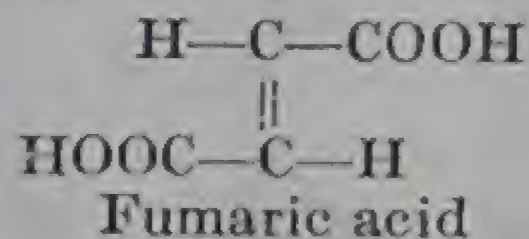
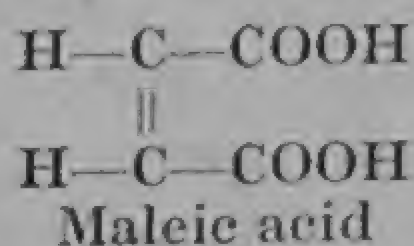


For the sake of convenience, these configurations are represented by projection formulæ as follows :—

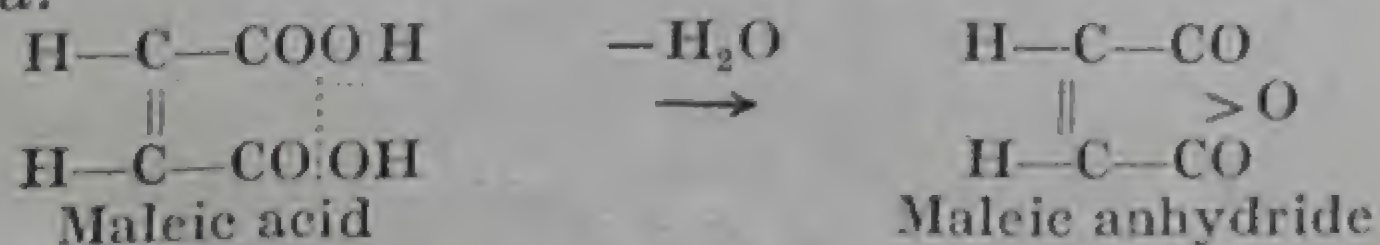


Compounds represented by configuration (1), *i.e.*, those in which similar groups lie on the same side of the molecule, are known as the *cis*-isomers, while those represented by configuration (2), having similar groups on opposite sides, are called *trans*-isomers.

The most familiar example of the *cis-trans*-isomerism or geometrical isomerism of this kind is that of maleic acid and fumaric acid :



The two acids possess different physical constants. Moreover, they behave differently when heated. Maleic acid, on being heated, readily loses a molecule of water, yielding an anhydride, while fumaric acid does not. When the latter is strongly heated it is partially converted into the anhydride of maleic acid. Because of the ready formation of the anhydride, maleic acid is assigned the *cis*-formula and fumaric acid the *trans*-formula.



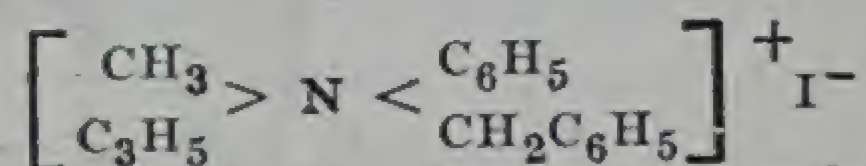
Other derivatives of ethylene, containing two *different* groups linked to each doubly bound carbon atom, also show geometrical isomerism (*e.g.*, dimethylethylenes, $CH_3.CH=CH.CH_3$ and crotonic and isocrotonic acids, $CH_3.CH=CH.COOH$).

The geometrical isomers of the ethylene series are interconvertible under certain conditions. Thus, when an aqueous solution of maleic acid is heated with a small quantity of hydrochloric acid, it gets transformed into fumaric acid.

*63. **Stereochemistry of Nitrogen.** There are two groups of stereo-isomeric nitrogen compounds, which are exactly analogous to the two classes of stereo-isomeric carbon compounds already described:—

(1) **Optically Active Nitrogen Compounds.** Although the three valencies of the trivalent nitrogen atom appear not to lie all in the same plane, all attempts to prepare optically active compounds of the general formula $Nabc$ have hitherto failed. It must, therefore, be concluded that the system is sufficiently mobile to bring about rapid racemization.

The compounds derived from tetra-covalent nitrogen, however, do exhibit optical isomerism. The case appears to be parallel to that of the compounds containing an asymmetric carbon atom. The substituted ammonium salts of the general formula $NabcdX$ occur in two optically active forms of equal and opposite rotation, and an inactive racemic form containing equimolecular quantities of the *d*- and *l*-forms. Thus in 1899 Pope and Peachey resolved *methyl-allyl-phenyl-benzyl-ammonium iodide*,



by fractional crystallization of its *d*-camphorsulphonates from a non-hydrolysing solvent (ethyl acetate or acetone). The *d*-camphorsulphonate of the *d*-base proved to be the less soluble salt. This and the *d*-camphorsulphonate of the *l*-base were obtained pure. The two salts, on being separately treated with potassium iodide, gave the sparingly soluble substituted ammonium iodide, which had a specific rotation of approximately $\pm 52^\circ$ in chloroform.

When a chloroform solution of the substituted ammonium iodide is warmed or allowed to stand for a few days, racemization takes place. This appears to be due to the dissociation of a molecule of the iodide followed by recombination in a different manner.

Several other compounds of the general formula $NabcdX$ have been resolved by different investigators.

Another class of optically active nitrogen compounds, namely the amine oxides of the general formula $\text{O} \leftarrow \text{NR}_1\text{R}_2\text{R}_3$, have been prepared and resolved by Meisenheimer.

A third class of optically active nitrogen bases, namely the substituted quaternary azonium bases of the general formula $[\text{NR}_1\text{R}_2\text{R}_3(\text{NH}_2)]\text{OH}$, have been prepared and resolved by the well-known Indian chemist, Bawa Kartar Singh.¹

According to modern views, the nitrogen atom in the ammonium and substituted ammonium compounds is tetravalent and not

¹ J.C.S. 1913, 103 ; 604 ; 105, 1972 ; 1920, 117, 1202.

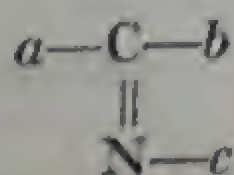
pentavalent as was formerly supposed. The four valencies of the nitrogen atom, like those of the tetravalent carbon, are supposed to be directed towards the four angular points of a regular tetrahedron, at the centre of which the nitrogen atom itself lies. The stereochemistry of nitrogen is therefore strictly analogous to that of carbon.

BAWA KARTAR SINGH,
M.A., Sc.D., F.I.C.,

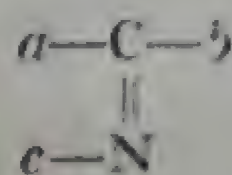
a member of the Indian Educational Service. He is a well-known organic chemist, and has done valuable work in the field of Stereochemistry. He has also developed a new method for the preparation of tertiary amines.



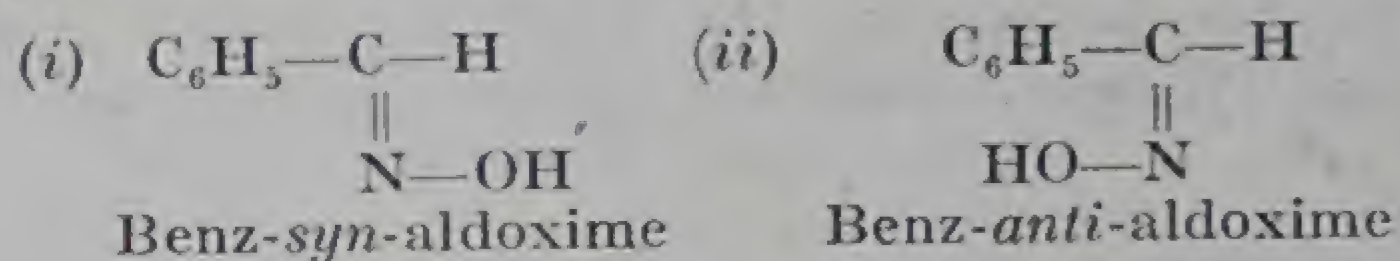
(2) Nitrogen Compounds Showing Geometrical Isomerism. Starting from the consideration that a very large number of organic compounds exist in which a trivalent nitrogen atom takes the place of a CH group (*e.g.*, benzene, C_6H_6 , and pyridine, C_5H_5N) Hantzsch and Werner came to the conclusion that the three nitrogen valencies occupy relative positions which are similar in direction to the three free valencies in the CH-group. Hence, when two nitrogen valencies are bound to one carbon atom, there results a case of geometrical isomerism which is exactly analogous to that of ethylene derivatives (Sec. 62) and which may be expressed by the following space formulæ:—



and



Numerous examples of this type of isomerism have been found among unsymmetrical oximes. Thus, benzaldoxime exists in the following two forms :—

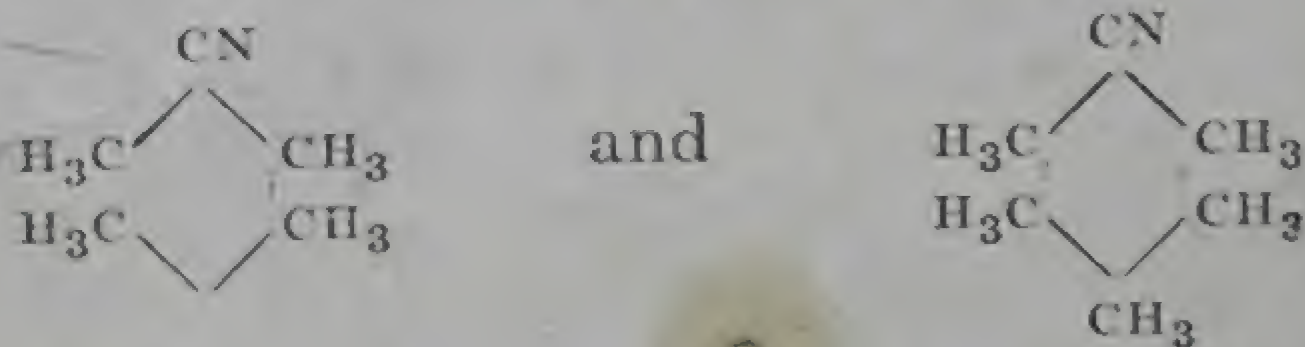


The determination of configuration of the stereoisomeric aldoximes is based on the principle of intermolecular reaction between groups, which are spatially contiguous. One of the forms, on being treated with acetic anhydride, loses water, yielding a nitrile, while the other is more stable and gives an acetyl derivative. The former is supposed to be the *syn*-isomer and the latter the *anti*-isomer.

As to the configurations of the stereoisomeric ketoximes, conflicting views are held, and for the present the problem remains unsolved.

64. Steric Hindrance. This is a stereochemical phenomenon unconnected with isomerism. It refers to the *influence exerted on a reacting group by the spatial disposition of neighbouring atoms*.

The first case of steric hindrance was discovered by Hofmann in 1872. It was found that certain aromatic tertiary amines, $\text{R}_1\text{R}_2\text{R}_3\text{N}$, where R_1 , R_2 , and R_3 are larger groups, will not react with methyl iodide to form quaternary ammonium salts. In 1884, Hofmann found that tetramethyl- and pentamethyl-benzonitriles,

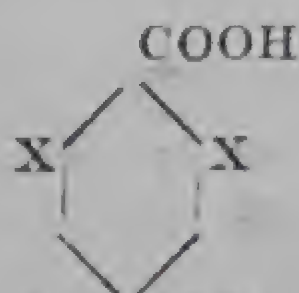


cannot be hydrolysed by the usual reagents. Since then, a large number of cases of steric hindrance have been observed by various investigators, and an explanation of this phenomenon has been offered.

It is assumed that each atom in a molecule vibrates about a certain mean position, and that the amplitude of the vibration is quite appreciable when compared with the size of the molecule itself. If this be so, the atom will require for its vibration a space somewhat larger than its own volume. It is quite easy to see that if another atom were to force its way into the vibration sphere of the first atom, collisions between the two will occur with the possible result that one of them is driven back. The case is similar to that of a person trying to force his way into a crowded room.

Now, in the case of a chemical reaction two or more groups are involved. These will react with one another only if they come within range of each other's attractions. If we surround one of the groups with such a mass of atoms that the other group or groups concerned in the reaction are unable to force their way in, we shall be able to hinder the progress of the reaction. Thus in the case of tertiary amines, studied by Hofmann, the nitrogen atom is surrounded by groups (R_1 , R_2 and R_3) that are of such a size as not to permit the methyl group of methyl iodide to come near the nitrogen atoms. Hence, no combination occurs. Similarly, the CN-group in tetramethyl- and pentamethyl-benzonitriles is protected from reaction by the crowding round it of the methyl groups.

Victor Meyer in 1894 found that di-*ortho*-substituted benzoic acids of the formula,



in which X stands for CH_3 , Cl, Br, NO_2 , etc., form no ester (or very little of it) when treated with alcohol and hydrogen chloride. Further, if such an acid is once converted into its ester by other means (*e.g.*, by the inter-action of its silver salt with an alkyl-iodide), the ester can be hydrolysed only with extreme difficulty.

QUESTIONS

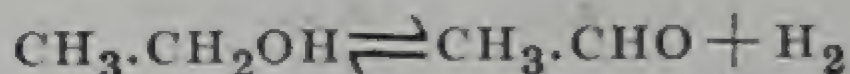
1. Write an account of Pasteur's work on tartaric acids.
2. Explain Le Bel and van't Hoff's theory of molecular configuration and show how it can account for the existence of the different varieties of tartaric acid. (*Calcutta, B.Sc., 1934*)
3. Write a short note on "Physiological Distinction between Optical Antipodes."
4. Write a short essay on the stereo-isomerism of organic compounds. (*B.Sc., Hons., 1924*)
5. Give various methods that have been used for the resolution of racemic compounds
6. Write notes on : (a) Asymmetric carbon atom ; (b) Asymmetric synthesis ; (c) Racemization ; (d) Optical inversion.
7. Write an account of Geometrical Isomerism of Carbon Compounds.
8. Write an essay on the Stereochemistry of Nitrogen.
9. Write a note on Steric Hindrance. (*Punjab, B.Sc., 1925 ; 1930 ; B.Sc., Honours School, 1929*)
10. How is it that tartaric acid when synthesized in the laboratory is optically inactive, whereas the same occurs as an optically active compound in nature ? How will you prepare the optically active form of the acid from the synthesized product ? Describe the various methods for resolving the inactive compound into its optically active components. (*Punjab, B.Sc., 1935*)

CHAPTER IX

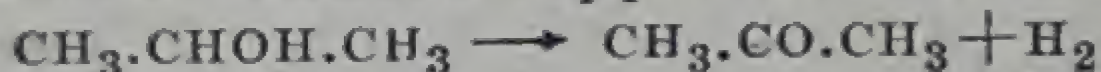
CATALYTIC ORGANIC REACTIONS

65. For a general discussion of the phenomenon of catalysis, characteristics of a catalytic action, and theories of catalysis, the reader is referred to a text-book of general chemistry¹. We shall here take up the applications of catalysis in various organic reactions :—

(1) **Oxidation.** Most of the primary and secondary alcohols readily lose hydrogen when heated in contact with a catalyst. Thus, ethyl alcohol gives an 80-per cent yield of acetaldehyde when passed over zinc heated at 660° .

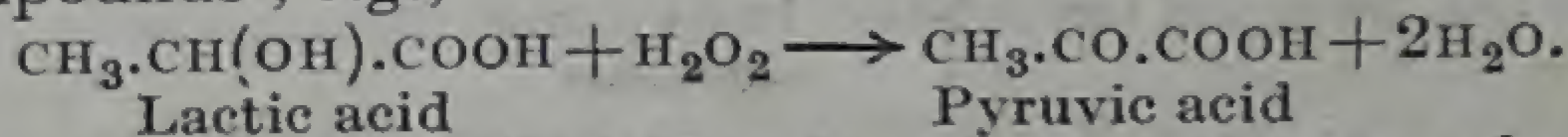


Isopropyl alcohol gives an almost quantitative yield of acetone when its vapour is passed over reduced copper heated at 250° to 320°C .



The oxidation of methyl alcohol to formaldehyde by air in the presence of finely divided platinum is another familiar example. An oxidation reaction of first rate commercial importance is the conversion of naphthalene into phthalic acid by fuming sulphuric acid in the presence of metallic mercury or mercuric sulphate, or by air in the presence of vanadium pentoxide. In Kjeldahl's method for the estimation of nitrogen (Sec. 16) the addition of a catalyst (mercury, mercuric oxide, cupric sulphate or manganese dioxide) greatly facilitates the oxidation.

An important catalytic oxidation discovered by Fenton, who showed that hydrogen peroxide, in the presence of a small quantity of ferrous sulphate as catalyst, brings about the oxidation of certain organic compounds ; *e.g.*,



(2) Reduction. Catalytic reduction, *i.e.*, reduction by means of hydrogen in the presence of finely-divided metals, was thoroughly investigated by *Sabatier* and *Senderens* in the years 1897 to 1911. Of the various metals tried, nickel was found to be the most efficient. It is absolutely necessary that the metal be in an extremely fine state of division. This is accomplished by heating the metallic oxide in a current of hydrogen at a temperature of about 300°.

¹See *e.g.*, "An Introduction to Modern Physical Chemistry," N. Singh and J. Singh (Atma Ram & Sons, Lahore).

The method of catalytic reduction has been found to be of very wide application. The substance to be reduced is usually vaporized, mixed with excess of hydrogen, and passed over finely-divided nickel heated at 150—250°.

Of the numerous reductions which have been effected by this process, the following few may be mentioned :

1. Ethylene to ethane :

Ni at 130—150°



2. Allyl alcohol to propyl alcohol :

Ni at 160—180°



3. Methyl isocyanide to dimethylamine :

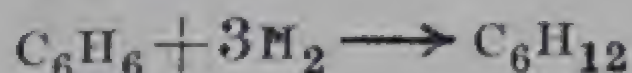
Ni at 160—180°



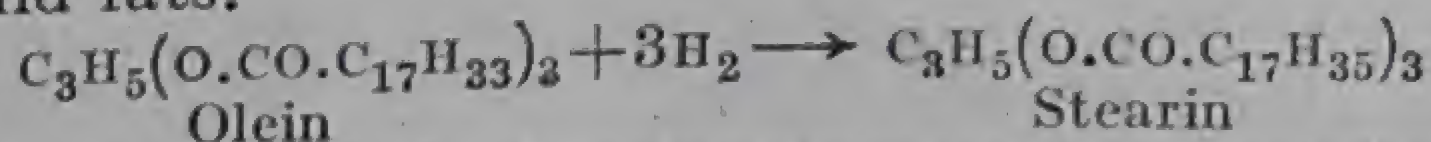
4. Nitromethane to methylamine :



5. Benzene and its homologues to hexahydrobenzene and its homologues :



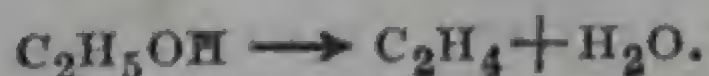
6. The method of catalytic reduction is nowadays extensively employed on a commercial scale for the manufacture of *margarine* and *artificial ghee* by the hydrogenation of oils. The process consists in passing hydrogen through the heated oil in which finely-divided nickel has been suspended. The unsaturated liquid glycerides are thereby converted into the corresponding saturated compounds, which are solid fats.



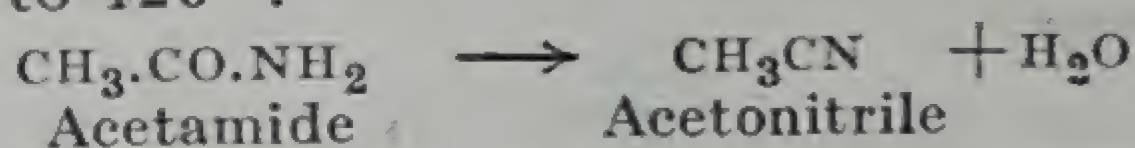
Metals other than nickel are sometimes used in catalytic reduction by means of hydrogen. Thus *Rosenmund* in 1918 employed finely-divided platinum (or palladium) precipitated upon an inert material (such as BaSO_4) for the catalytic reduction of acid chlorides to aldehydes :



(3) Dehydration. Many organic substances containing hydrogen and oxygen lose the elements of water when their vapours are passed over heated aluminium oxide, phosphate or silicate. Thus, when ethyl alcohol is passed over aluminium oxide heated to about 400°, it yields ethylene :



Another example of catalytic dehydration is the conversion of an amide into a nitrile when the vapour of the former is passed over aluminium heated to 420° :

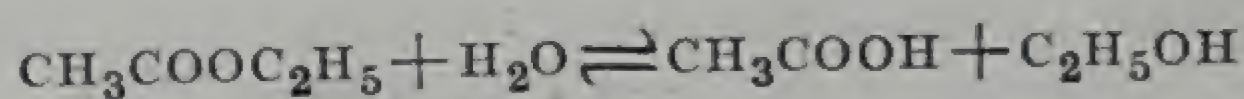


(4) Alkylation of Ammonia. See under Sec. 307.

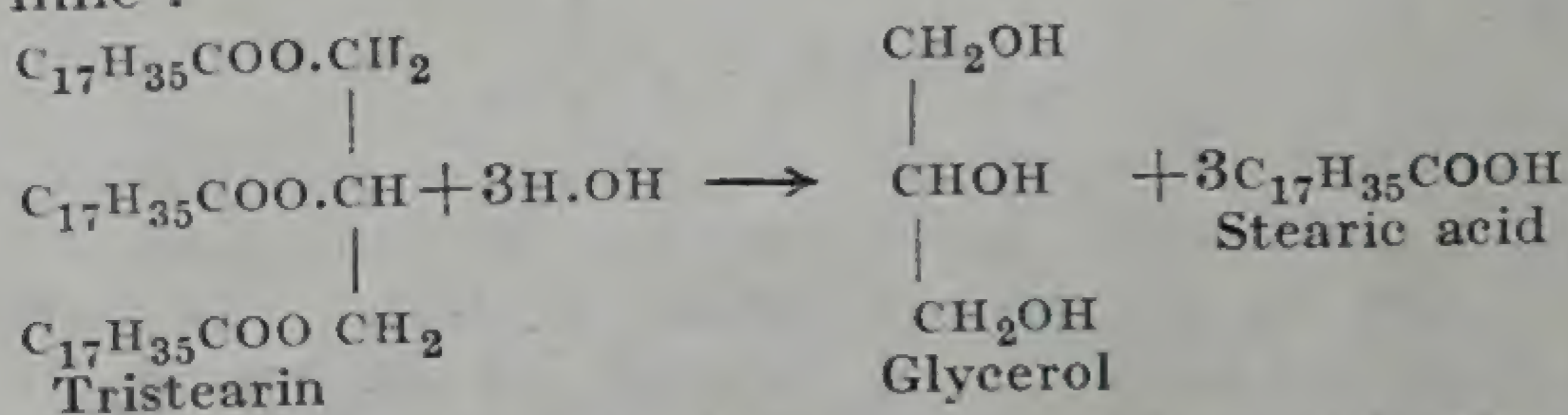
(5) Esterification. *Sabatier* and *Maihle* have shown that when a mixture of molecular proportions of an alcohol and an acid in the vaporous state is passed over a column of titanium dioxide kept at $290-300^{\circ}$, a 70 per cent yield of the ester is obtained. The process has been found to be extremely rapid.

(6) Hydrolysis. The following cases exemplify the hydrolytic decomposition of organic substances under the influence of catalysts :—

(i) Hydrolysis of an ester in the presence of a mineral acid or an alkali



(ii) Hydrolysis of fats and oils by superheated steam in the presence of a little lime :



A new method for effecting the hydrolysis of fats and oils is by means of the Twitchel reagent (sulpho-benzene-stearic acid).

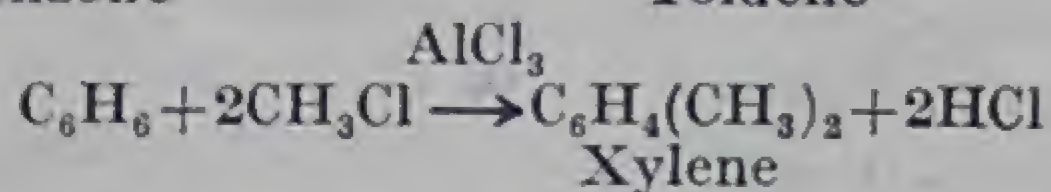
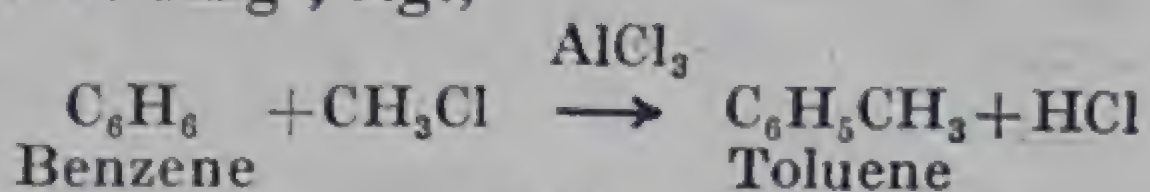
(iii) Hydrolysis of acid amides and acid nitriles in the presence of mineral acids or aqueous alkalies.



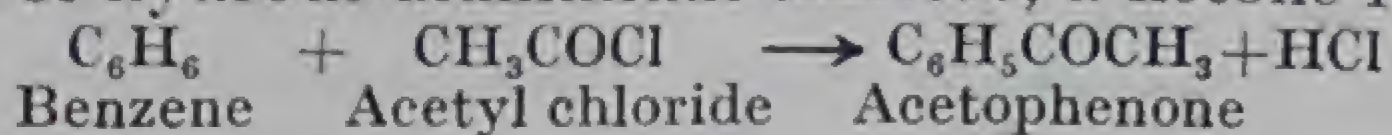
(7) Friedel and Crafts' Reaction. This is a very important catalytic reaction in which anhydrous aluminium chloride is used as a catalyst. It is employed for the preparation of homologues of benzene and certain other aromatic compounds. The following are the more important examples of the use of this reaction :—

(i) When a benzene hydrocarbon is treated with an alkyl halide in the presence of anhydrous aluminium chloride, the alkyl group

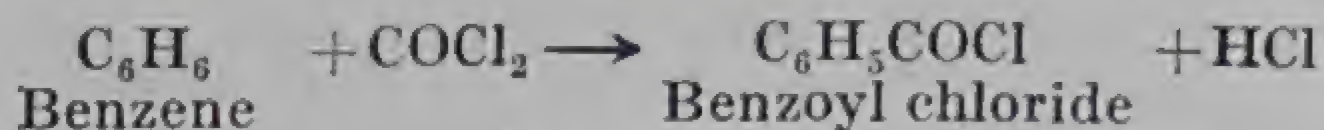
enters the benzene ring ; *e.g.*,



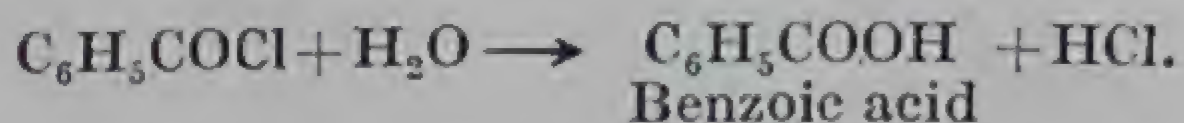
(ii) When an acid chloride is added to a benzene hydrocarbon in the presence of hydrous aluminium chloride, a ketone results ; *e.g.*,



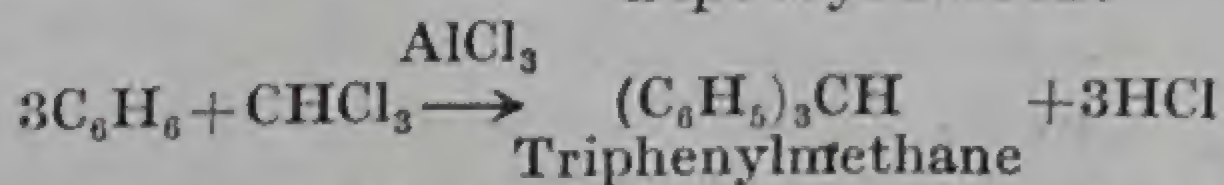
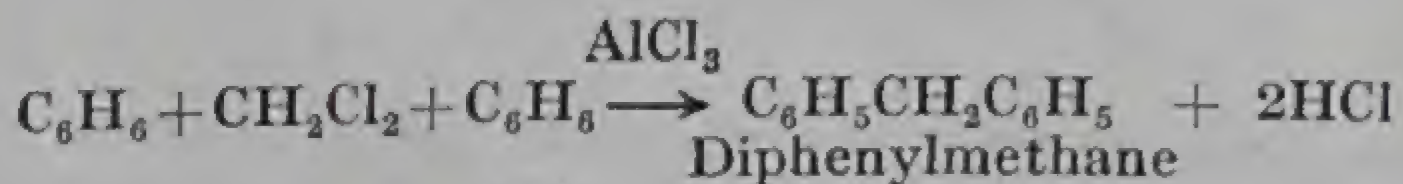
(iii) When a benzene hydrocarbon is treated with phosgene gas, in the presence of anhydrous aluminium chloride, an acid chloride is produced,



The acid chloride, on being decomposed with water, gives a carboxylic acid.



(iv) Formation of *diphenylmethane*, by the interaction of methylene chloride and benzene, and of *triphenylmethane*, by the interaction of chloroform and benzene, are other examples of Friedel and Crafts' reaction.



The above are but a few of a countless number of catalytic reactions taking place in the realm of organic chemistry. The assimilation of carbon dioxide by plants in the presence of chlorophyll and sunlight, the assimilation of food by animals, the process of respiration, and numerous other anabolic and catabolic changes taking place in the plants and animals are practically catalytic in nature. Numerous other examples of catalytic organic reactions will be met with in the following chapters.

66. Fermentation and Enzyme Action. It is a matter of common experience that vegetable and animal matter, particularly when moist, undergoes certain slow chemical changes by which the highly complex substances get gradually decomposed into simpler and still simpler compounds, until, finally, in most cases, carbon dioxide, ammonia and water are produced. Souring of milk and kneaded flour, production of wine and vinegar, rotting of wood and vegetables,

and putrefaction of meat, etc. are well-known examples of the changes of the above, type, which are collectively called *fermentation processes*.

Fermentation processes are brought about by certain living organisms, called **ferments**. The action of ferments is due to the presence in their cells of complex nitrogenous substances, called **enzymes**, which act catalytically.

The enzymes are extraordinarily *specific* in their action as catalysts. They are very sensitive to temperature changes and are usually destroyed at about 70°C . The *optimum temperature*, i.e., the temperature at which they are most active, lies between 25° and 36°C . Fermentation processes are exothermic in nature, the energy set free during the reaction is utilized by the ferment concerned, for its growth.

The simplest example of fermentation is that of sugar by yeast to form ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$. The yeast cells (Fig. 45) contain a number of enzymes, two of which, called **invertase** and **zymase**, are concerned in the alcoholic fermentation of sugar. The invertase first causes the hydrolytic decomposition of cane-sugar into glucose and fructose, which are then decomposed by zymase to form ethyl alcohol and carbon dioxide :

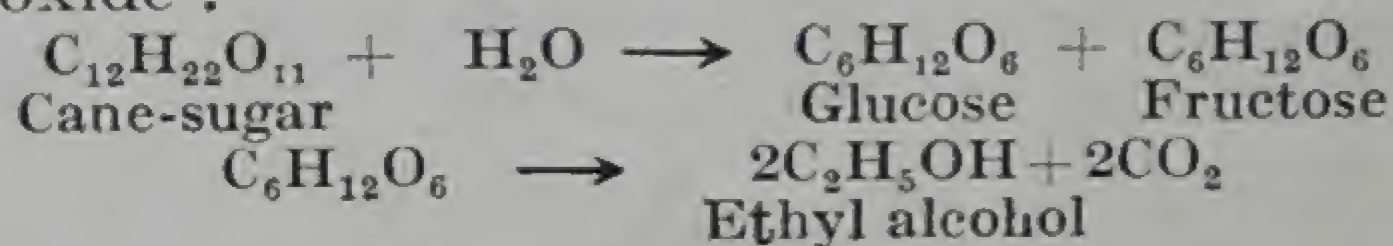


Fig. 45. Yeast cells (highly magnified).

Another familiar example is the lactic fermentation of milk. When a small quantity of curd (*jag*) is added to warm milk, the sugar present in the milk is converted, into lactic acid by a certain species of bacteria, called **lactic bacilli**. The lactic acid causes the coagulation of the albumen present in the milk, producing curd. On keeping, the curd goes sour because the lactic acid it contains is converted into butyric acid by the action of another ferment called **butyric bacillus**. The optimum temperature for the lactic fermentation is 34° to 35°C ; hence the necessity of adding the ferment to warm milk.

A number of other examples of fermentation will be dealt with at their proper places.

Theories of Fermentation. Pasteur, who carried out exhaustive researches on fermentation of sugar, held the view that fermentation is a purely physiological action and is absolutely dependent upon the life processes of the yeast cells. Liebig, on the other

hand, regarded the phenomenon as being of a purely chemical nature. Buchner carried out a series of experiments with a view to settling this point. He submitted yeast to strong pressure, thereby disrupting the cell walls and obtaining a juice. This was filtered in order to free it completely from adhering cells. The "expressed yeast juice," thus obtained, was found to set up fermentation in exactly the same way as the living yeast cells. He concluded that the yeast cells contained *enzymes*, or non-living complex substances capable of bringing about fermentation. The yeast cells are, therefore, responsible for fermentation only so far as they generate enzymes. Buchner also showed that the other fermentation processes, such as souring of milk, are not caused by the micro-organisms themselves but by the enzymes they contain.

QUESTIONS

1. Give an account of the use of catalytic agents in organic chemistry. *Kissam Devi*
(Punjab, B.Sc., 1921)
 2. What do you know of *fermentation processes*? Name any six organic compounds which are produced by this process, and describe the manufacture by fermentation of any *one* of them. (Punjab, B.Sc., 1926)
 3. Write notes on: (i) Catalytic reduction, (ii) Friedel and Crafts' reaction and (iii) Enzyme action.
- Q. 1098*
Q. 1099

From page 82 to 118 Not in the course

PART II

ALIPHATIC OR OPEN-CHAIN COMPOUNDS

CHAPTER X

SATURATED HYDROCARBONS OR PARAFFINS

68. Aliphatic Compounds. The numerous substances classified as *aliphatic* or *fatty* compounds may be regarded as derived from methane, CH_4 , the first member of the homologous series of saturated hydrocarbons dealt with in this chapter. The name "aliphatic" refers to the inclusion in this group of the animal and vegetable fats. In respect of molecular constitution, the compounds of the class are distinguished by their having *open* carbon chains in contrast to the closed carbon chains or rings of the "aromatic" series.

69. General Formula and Nomenclature of Paraffins. The hydrocarbons of the paraffin series possess the general formula $\text{C}_n\text{H}_{2n+2}$. The names of the various members of this series end in *-ane*, and are derived from the Greek numerals indicating the number of carbon atoms in the molecule. The following are a few of the first members of the series :—

NAME	FORMULA	NUMBER OF ISOMERIDES
Methane	CH_4	1
Ethane	C_2H_6	1
Propane	C_3H_8	1
Butane	C_4H_{10}	2
Pentane	C_5H_{12}	3
Hexane	C_6H_{14}	5
Heptane	C_7H_{16}	9
Octane	C_8H_{18}	18

70. Physical Properties. The physical properties of paraffin hydrocarbons show a gradual change. The first four members of the series are gaseous, while those containing from 5 to 16 carbon atoms are colourless liquids. The higher members are colourless solids. The boiling-point rises regularly as the series is ascended, but the difference between the boiling-points of consecutive hydrocarbons gradually diminishes.

For isomeric hydrocarbons, the following general statements as regards the boiling-point may be made :—

- (1) *The longer the chain the higher the boiling-point ;*
- (2) *For the same length of chain, the nearer the substituents to the middle of the chain, the higher the boiling-point.*

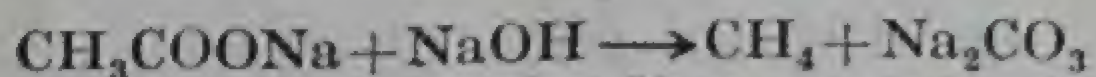
71. Chemical Properties. The paraffin hydrocarbons are characterized by their lack of chemical activity ; hence the name (Latin *parum*, little and *affinis*, affinity). They are neutral in character and not affected by most of the reagents excepting the halogens (see under *Methane*, Sec. 72). They do not react with oxygen at ordinary temperatures ; but at higher temperatures, they are readily oxidized, and oxidation, when once started, is difficult to control. It is only recently that a beginning has been made in the preparation of certain products by the direct oxidation of aliphatic hydrocarbons.

General Methods of Formation. See under *Ethane*, Sec. 73.

72. Methane. *Marsh Gas*, CH_4 .

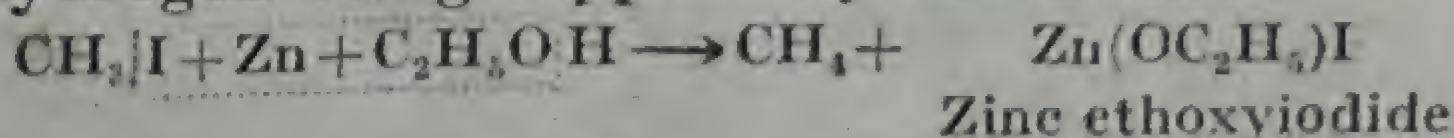
Occurrence. Methane is produced in considerable quantities when cellulose and other organic matter undergoes putrefaction under stagnant water. On this account, the gas is found in marshy places ; hence the name *marsh gas*. The *natural gas* that issues from the earth in petroleum districts consists of methane and its homologues. Methane also issues from seams in coal-mines, where, by diffusing into the air, it forms an explosive mixture hence the name *fire-damp* given to it by coal-miners. Methane is an important constituent of *coal gas*, in which it is present between 30 and 40%.

Preparation. (1) Methane is most conveniently prepared in the laboratory by heating anhydrous sodium acetate with soda-lime. The active constituent of soda-lime in this reaction is sodium hydroxide, but the pure alkali is not employed, owing to its being deliquescent and easily fusible.

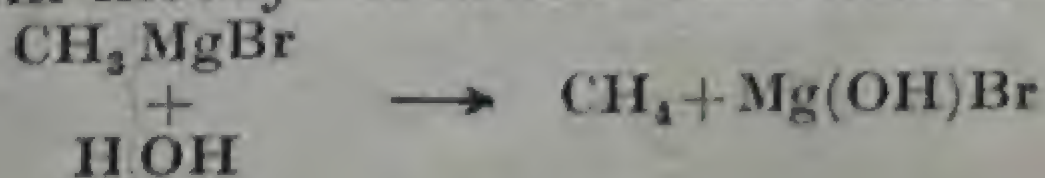


Expt. 20. Heat a mixture of *fused* sodium acetate (1 part) and powdered soda-lime (4-parts) in a copper tube provided with a delivery tube. Collect the issuing gas over water.

(2) Pure methane is most readily obtained by the reduction of methyl iodide by means of alcohol and zinc-copper couple (See Exp. 22), the hydrogen being supplied by the alcohol,



(3) Another method of preparing pure methane is by the decomposition of magnesium methyl bromide with water.

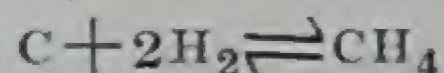


(4) Methane may be obtained in the laboratory from aluminium carbide, Al_4C_3 , which, when boiled with water, yields the gas contaminated with hydrogen (20 per cent) and other impurities.



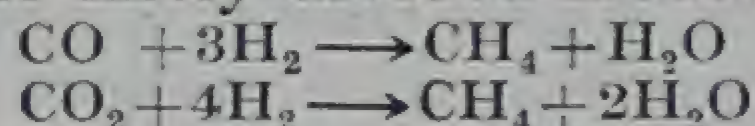
Synthesis¹. Methane has been synthesized by the following reactions :—

(1) When a current of hydrogen is passed over carbon heated at $1,200^\circ$, the elements combine together to yield a small proportion (1 per cent) of methane :—



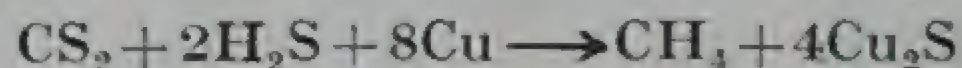
the reaction is reversible, since when pure methane is heated at $1,200^\circ$, about 99 per cent of it is decomposed into its elements. If carbon be intimately mixed with finely-divided nickel, its combination with hydrogen occurs at lower temperatures and much larger amounts of methane are formed.

(2) Sabatier and Senderens have obtained an almost quantitative yield of methane by passing a mixture of hydrogen and carbon monoxide or dioxide over finely-divided nickel at 250° to 300° :



The process has commercial possibilities in localities where natural gas is not available.

(3) The earliest synthesis of methane was effected by Berthelot by passing a mixture of carbon disulphide vapour and hydrogen sulphide over heated copper :



Physical Properties. Methane is a colourless gas with a slight odour. It can be liquefied at 11° under a pressure of 180 atmospheres. It is very slightly soluble in water, 100 c.c. of water at 4° dissolving 5 c.c. of the gas.

Chemical Properties. Methane, like other hydrocarbons of this series, is characterized by its inertness and stability. It is neutral in character, and is not affected by acids or alkalies. Nor is it affected by oxidizing agents such as nitric acid, potassium permanganate or dichromate. The only important reactions of methane are :

(1) *Combustibility.* Methane burns in air with practically a non-luminous flame, forming carbon dioxide and water.



When mixed with air or oxygen and ignited, the gas explodes violently. Mixtures of methane and air occurring in coal mines are of constant danger to miners.

¹The "complete synthesis" of a compound means its formation from the component elements, or from simpler compounds already obtained from their elements.

(2) *Action of Chlorine.* Methane is a "saturated" compound and can give rise only to substitution products. When it is mixed with chlorine or bromine vapour, there is no action in the dark; but on exposing the mixture to sunlight, an interaction occurs with explosive violence. The four hydrogen atoms of the methane molecule are successively replaced by chlorine with the production of the following four substitution products :—

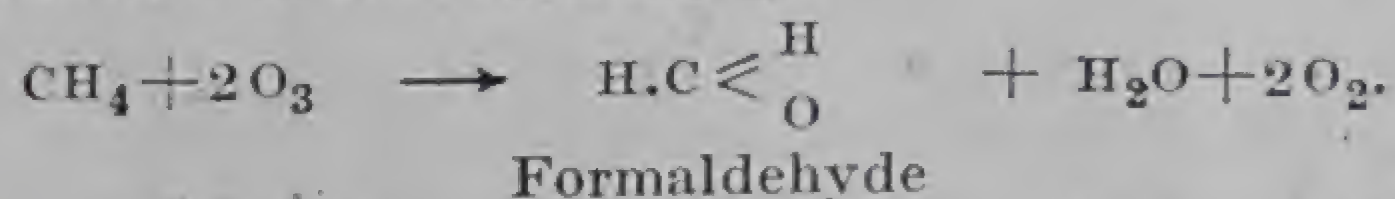
Chloromethane, or methyl chloride, CH_3Cl .

Dichloromethane, or methylene chloride, CH_2Cl_2 ,

Trichloromethane, or chloroform, CHCl_3 ,

Tetrachloromethane, or carbon tetrachloride, CCl_4 .

(3) *Reaction with Ozone.* When methane is treated with ozonized oxygen two of its hydrogen atoms are exchanged for an oxygen atom with the production of formaldehyde.



This reaction constitutes a delicate test for methane, since even small quantities of formaldehyde may be readily identified by its characteristic reactions (*q. v.*).

(4) *Reaction with steam.* See under Sec. 79.

Expt. 21. (a) Burn a cylinder full of methane. Notice that the flame is non-luminous. Test the gas left in the cylinder with lime-water; the latter turns milky.

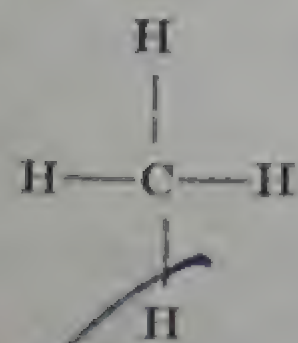
(b) Pass the gas through (i) bromine water, (ii) sodium hydroxide solution rendered pink with phenolphthalein (iii) dilute sulphuric acid, rendered pink with methyl orange, and (iv) potassium permanganate solution, acidified with sulphuric acid. Notice that there is no appearance of reaction with any of these reagents.

(c) Fill a strong "soda water" bottle one-third with methane and two-third with oxygen, and then bring its mouth near the flame (Fig. 46). A powerful and very loud explosion will occur.



Fig. 46.

Composition. Methane being a gaseous hydrocarbon, its composition can be determined by the method explained under Sec. 27.



Constitution. Since carbon is tetravalent and hydrogen monovalent, the methane molecule must be represented by the constitutional formula shown in the margin.

73. Ethane. C_2H_6 . This occurs along with methane in the natural gas, and is also found dissolved in petroleum.

Preparation. 1. Ethane may be obtained by reactions 1, 2 and 3 used for methane, sodium propionate, $\text{C}_2\text{H}_5\text{COONa}$, being used in reaction 1, and ethyl iodide and ethyl magnesium bromide in reactions 2 and 3 respectively.

Expt. 22. Preparation of Ethane from Ethyl Iodide. Take 20 grams of granulated zinc in a beaker, and cover it with a 2 per cent solution of cupric sulphate. Allow to stand, until the blue colour is discharged; then pour off the solution. Repeat the above treatment with cupric sulphate three or four times.

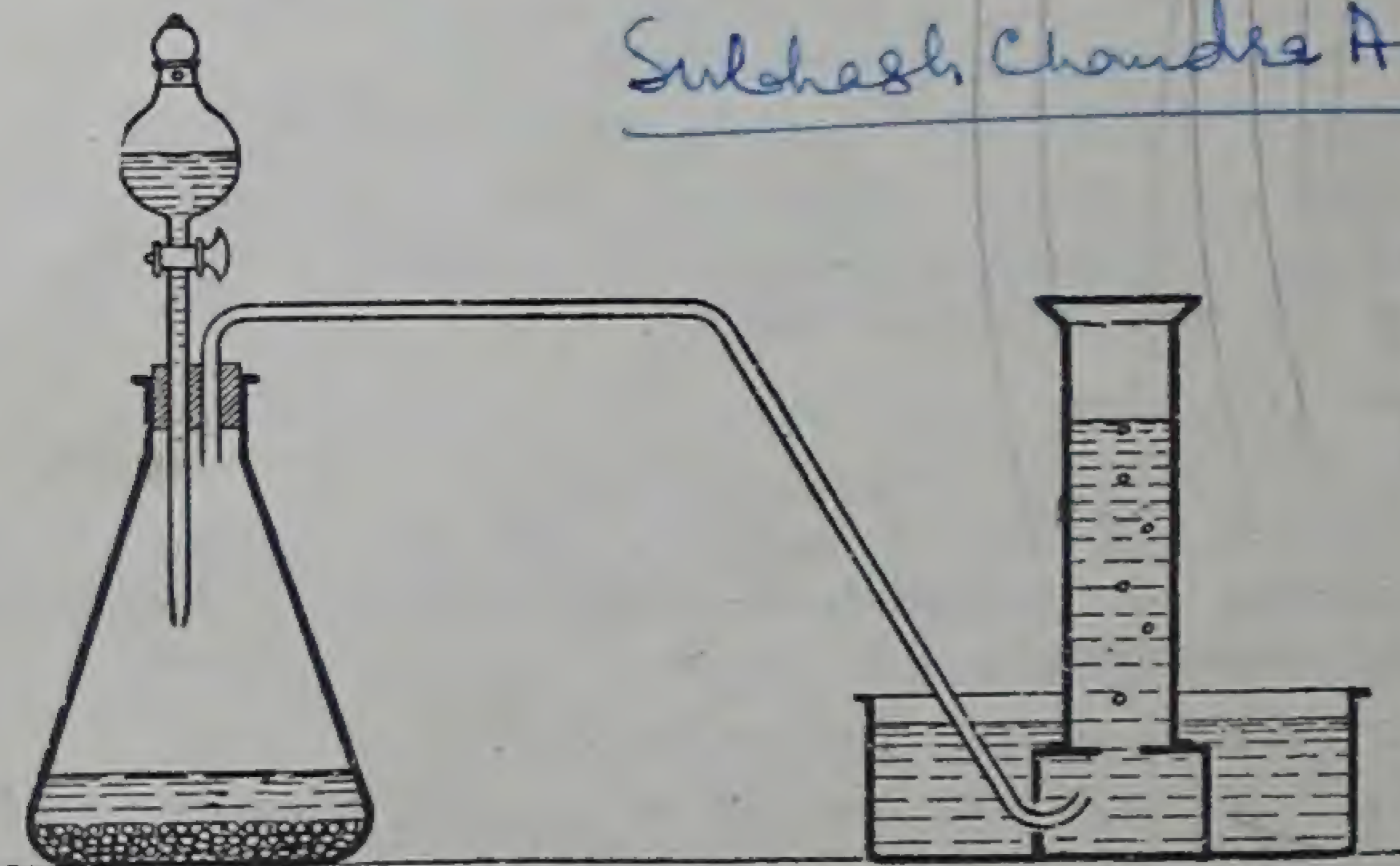


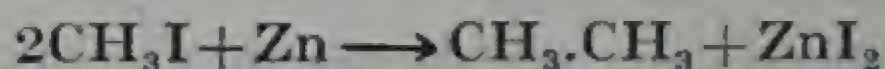
Fig. 44. Preparation of Ethane from Ethyl Iodide.

Wash the zinc-copper couple, thus obtained, with water and finally with a little alcohol. Then place it in a flask provided with a delivery tube (Fig. 44). Add to the flask 100 c.c. of alcohol mixed with a drop or two of dilute sulphuric acid, and then drop ethyl iodide into the mixture from the dropping funnel. Collect the gas evolved over water.

Study the properties of the gas as in the case of methane.

II. In addition to the above three methods, ethane may be obtained by the following reactions :—

(1) From *methyl iodide*, by heating with metallic sodium or zinc (Wurtz' reaction) :—

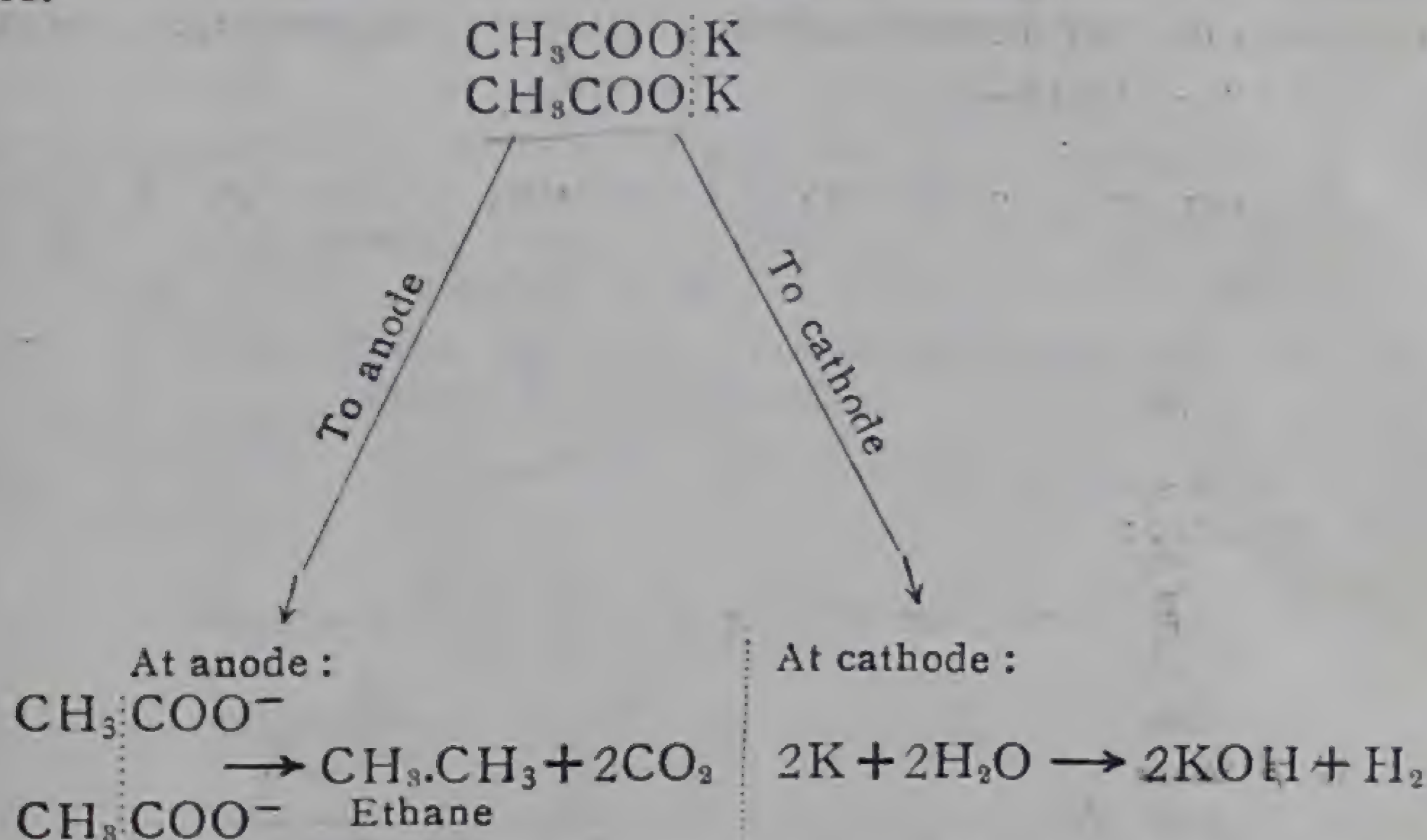


The reaction can be employed for synthesizing ethane from methane.

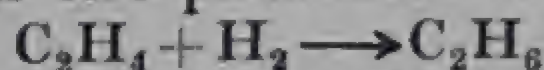
(2) By the electrolysis of a concentrated solution of potassium acetate (Kolbe's reaction). At the cathode, potassium ions are discharged. The liberated metal attacks the water present, forming potassium hydroxide and hydrogen. At the anode, the anions, CH_3COO^- , lose their charge, and immediately break up into CO_2 molecules and the methyl groups. The latter, being incapable of

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independent existence, combine together in pairs to form ethane molecule.



(3) Ethane has been prepared on a large scale by the combination of ethylene and hydrogen in the presence of finely-divided nickel :

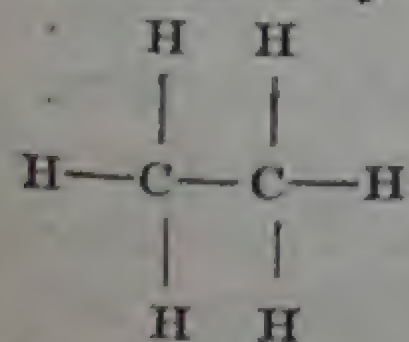


Note. The methods of formation described above for ethane are *general methods* that can be employed for preparing any other higher member of this series. Distillation of coal or wood yields volatile products containing a high proportion of paraffin hydrocarbons.

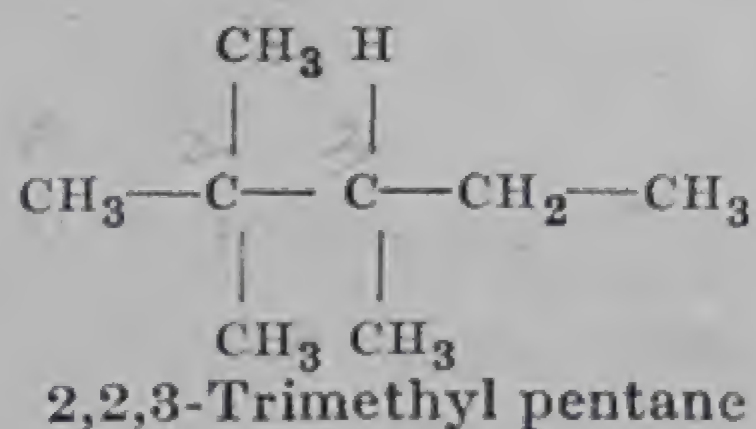
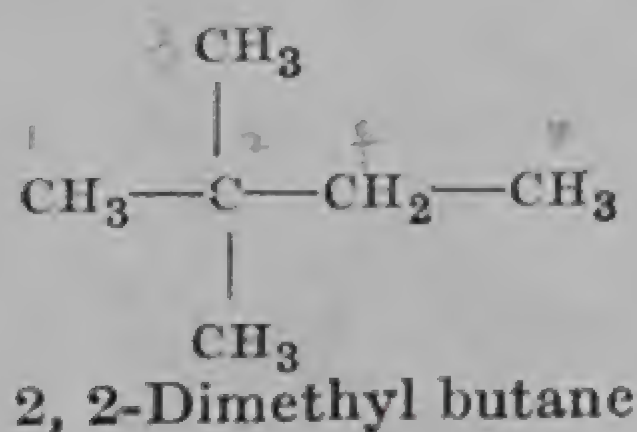
Properties. Ethane, like methane, is a colourless, tasteless gas. Its critical temperature is $+34^\circ$ and critical pressure 50 atmospheres. It is practically insoluble in water and slightly soluble in alcohol.

In its chemical properties, ethane closely resembles methane. It readily reacts with chlorine and bromine, yielding *substitution products* all the six hydrogen atoms being successively replaced by an equivalent quantity of chlorine or bromine. The *final* products are hexachloro-ethane, C_2Cl_6 , and hexa-bromo-ethane, C_2Br_6 , both of which are colourless, crystalline solids.

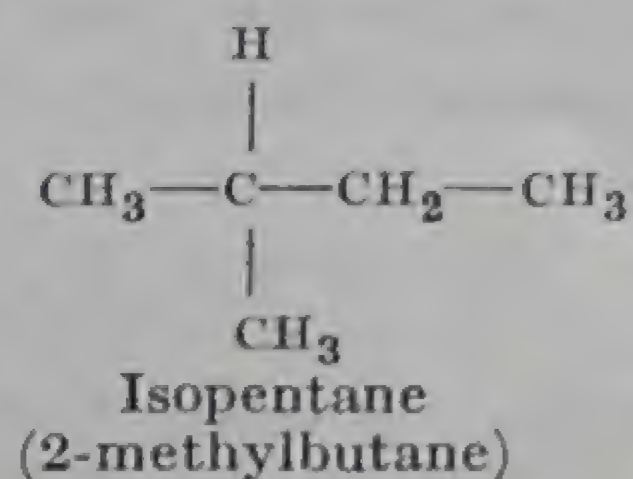
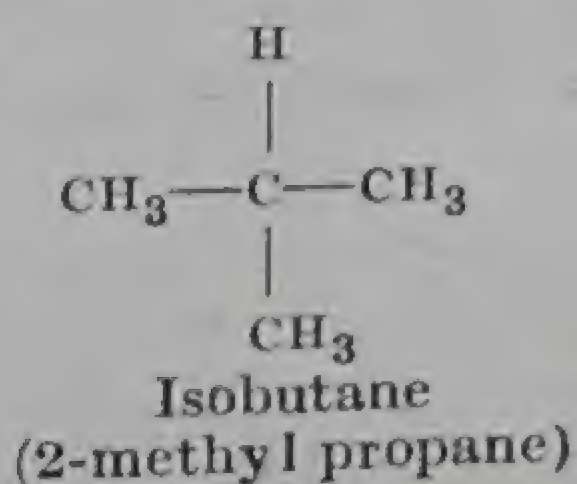
Constitution. Explosion with oxygen (Sec. 27) shows that the molecular formula of ethane is C_2H_6 . The two carbon atoms must be directly united, as a monovalent hydrogen atom could not possibly link them together. Moreover, since the carbon is tetravalent, the two carbon atoms must carry three atoms of hydrogen each. Hence, the structural formula of ethane is as shown in the margin. This view is confirmed by the formation of ethane from methyl iodide by Wurtz' reaction (Sec. 73).



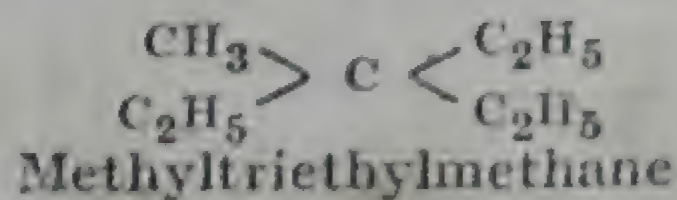
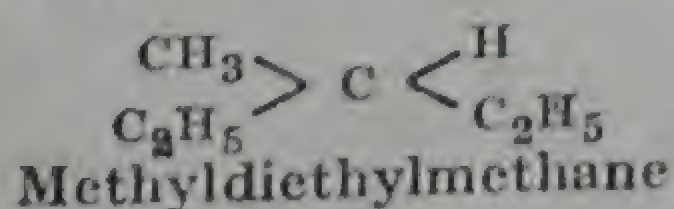
are derived from the Greek numerals indicating the number of carbon atoms in the molecule, and have the termination *-ane*. Thus C_5H_{12} is called *pentane*, C_6H_{14} *hexane*, C_7H_{16} *heptane*, and so on. In naming a hydrocarbon with a forked or branched chain, it is regarded as derived from the hydrocarbon having the *longest* unforked or normal chain present in the molecule. The carbon atoms of this chain are numbered consecutively, *commencing with the end nearest which a methyl side-chain is attached*. The position of each side chain is indicated by the figures used in numbering the carbon atoms in the normal chains, each figure being repeated as many times as there are side-chains. The method of nomenclature may be illustrated by the following examples :—



(2) In the older nomenclature, which still finds frequent use, the hydrocarbon with a straight chain is called *normal* and is designated by the prefix *n-*. The isomer with a methyl group attached to carbon No. 2 of a normal chain is called the *iso* compound. Thus 2-methylpropane and 2-methylbutane are called *isobutane* and *isopentane* respectively :—



Other isomers are named by regarding them as derived from methane by replacement of its hydrogen atom by various alkyl groups. In making the selection, that carbon atom is taken as belonging to the original methane molecule which carries the *largest* number of other carbon atoms. The following examples will serve to illustrate the method :—



76. Petroleum.

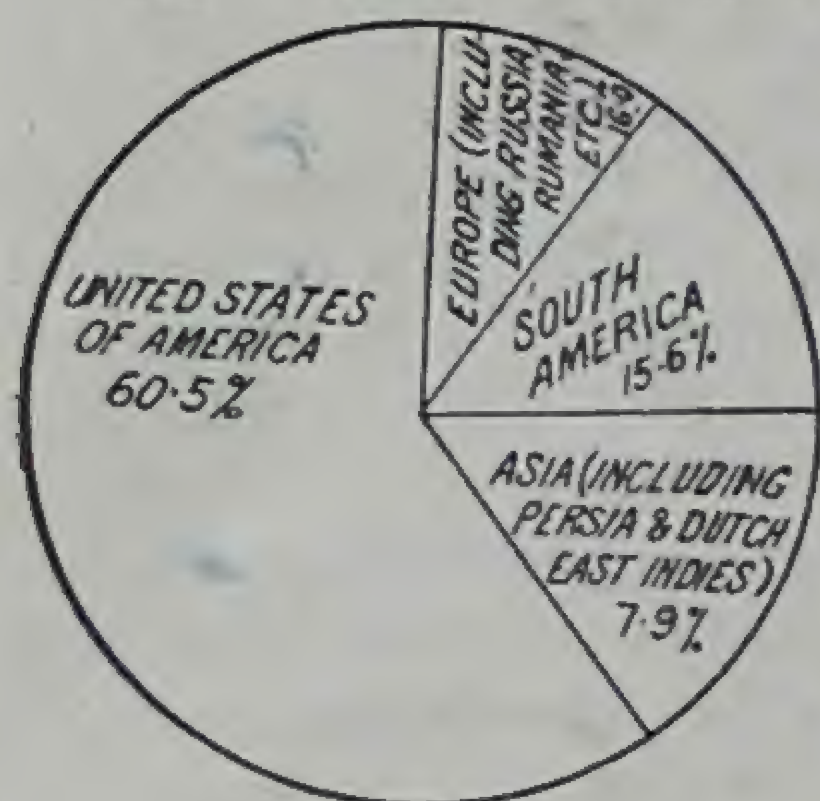


Fig. 48.

Petroleum production of various countries.

Occurrence. Petroleum occurs in many localities. The total annual production of the world is approximately 1,000,000,000 barrels.¹ Of this amount, the United States of America alone produces over 60 per cent. The estimated percentage figures for various countries are as shown graphically in Fig. 48.

British India contributes only 0.65 per cent of the world's production. The most important oil-fields in this country are those of Yenangyaung in Burma and Attock in the Punjab.

Physical Characters. Crude petroleum is a viscid, fluorescent liquid having a dark green, yellow or brown colour. It possesses usually an offensive odour owing to the presence of organic sulphur compounds.

Composition. Petroleum consists essentially of a mixture of hydrocarbons of the paraffin series together with cyclo-paraffins and hydrocarbons of the aromatic series; the actual composition, however, varies with the place of origin. The Pennsylvanian oil contains about twenty different hydrocarbons, most of which are of the paraffin series. The Russian oil, on the other hand, contains a large proportion of higher-boiling aromatic hydrocarbons, together with penta- and hexamethylenes (naphthenes). The low-boiling fractions of most petroleums consist mainly of the lower hydrocarbons of the paraffin series.

Origin. Two theories have been proposed as to the origin of petroleum, one *organic* and the other *inorganic*, both being supported by experiment. The Russian chemist Mendeleeff suggested that petroleum is formed by the action of water on metallic carbides present in the hot interior of the earth. This "inorganic" theory of the origin of petroleum was later supported by the work of Moissan, and of Sabatier and Senderens. However, the theory is so incompatible with the geological occurrence of oil that at the present day it commands little consideration.

Engler, in 1900, discovered that the destructive distillation, under pressure, of fats, such as fish oil, gave a product strongly resembling petroleum. This led him to put forward the hypothesis that petroleum is derived mainly from the remains of marine organisms. After the death of the organism, the nitrogenous content decomposed

¹ A barrel contains 42 gallons.

relatively quickly, leaving behind a fatty material which got slowly converted into petroleum under the influence of heat and pressure. The chief evidence in favour of the organic origin of petroleum is that it contains certain optically active substances. These are characteristic of materials formed by living organisms: their presence cannot be accounted for by assuming the inorganic origin of petroleum. Another fact that supports the organic origin of petroleum is the invariable presence in it of nitrogen and sulphur compounds.

Mining. Petroleum occurs at depths which vary within very wide limits. At Virginia and Ohio, the oil strata are from 50 to 60 feet deep; in Pennsylvania they are from 2,400 to 2,600 feet deep. Petroleum is brought to the surface by drilling wells through the

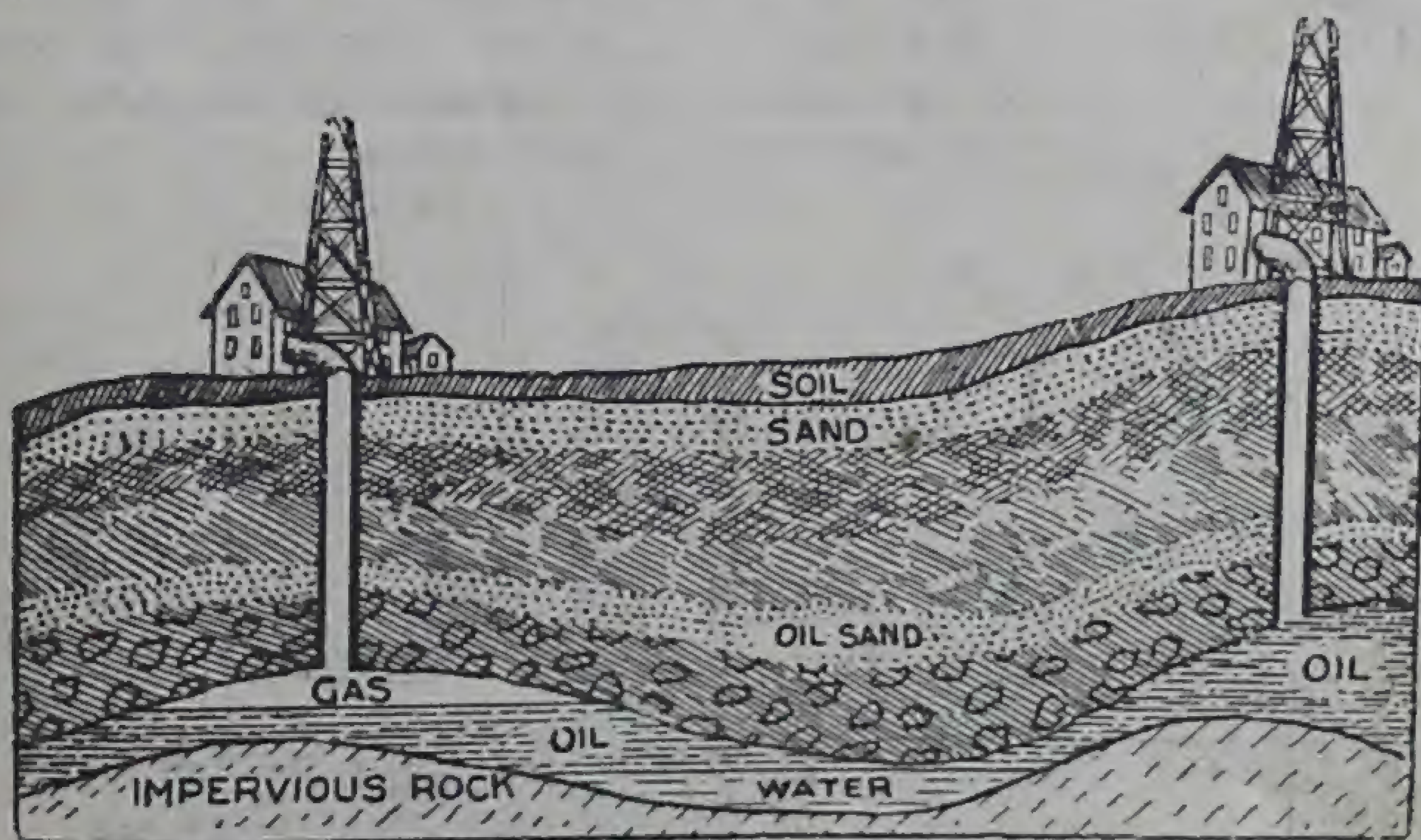


Fig. 46. Section through an Oil-field.

overlying strata into the oil-bearing sand-stone. A section through an oil-field is shown in Fig. 49. If a boring be made in the middle, we would get only salt water. In the two positions where the wells are shown to be drilled, we would get petroleum (right) and natural gas (left).

Many wells, particularly in newly-opened territory, where the original gas-pressure has not been lost, are flowing wells, known as "gushers." This spontaneous flow, however, soon declines, when pumping becomes necessary in order to maintain the production of oil.

Refining. Crude petroleum is generally not refined at the oil-field, but is sent to the refinery either through a pipeline or in tank ships. The Yenangyaung oil is refined at Rangoon by the Burma

Oil Company, Indo-Burma Petroleum Company, and other concerns. The Punjab oil is refined by the Attock Oil Company at Rawalpindi.

At the refinery, the crude petroleum is fractionally distilled in large size iron stills. Fig. 50 shows a horizontal still with two air-cooled condensers, *A* and *B*, from which the successive fractions pass through three coils of pipe immersed in tanks of cold water. The crude oil is continuously fed into the still at about the same rate as that of distillation. The high-boiling constituents (from $C_{16}H_{34}$ upwards), consisting of the *heavy oil* and *paraffin*, are condensed in the air-cooled tower *A*. The next fraction, *i.e.*, the one condensing in *B*, consists of the *kerosene oil* ($C_{10}H_{22}$ — $C_{15}H_{32}$). The uncondensed vapour of the lower hydrocarbons (C_4H_{10} — C_9H_{20}) leaving the condenser *B* are condensed in the last coil of pipe immersed in cold water. The fraction thus obtained is known as *naphtha*. The gaseous hydrocarbons (CH_4 to C_4H_{10}) that the crude oil contains in solution pass off uncondensed, and may be collected in gas-holders.

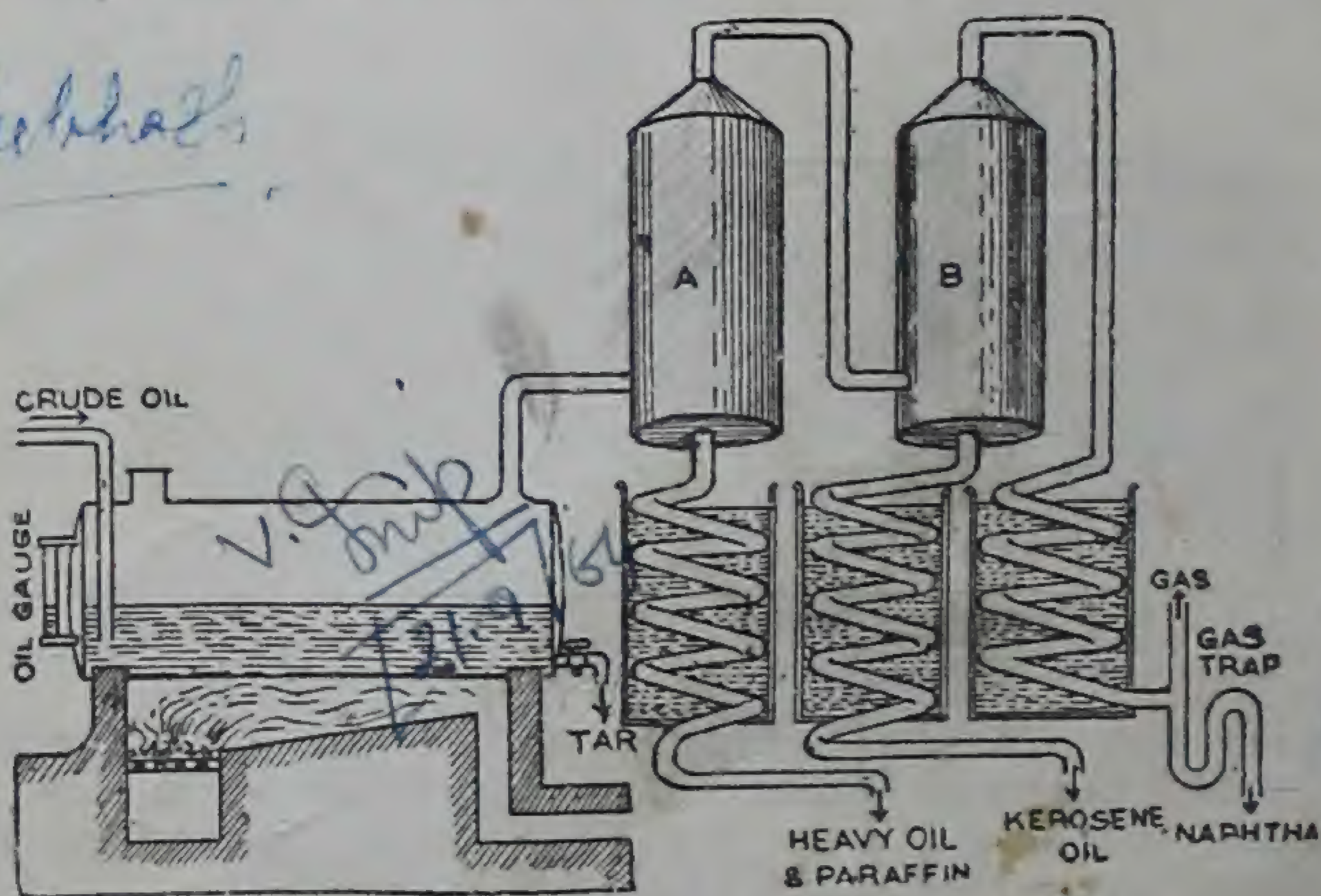


Fig. 50. A Horizontal Still for Continuous Fractional Distillation of Petroleum.

The different products obtained in the above process are put to the following uses:—

(1) *Naphtha*. This is carefully refractionated, and separated into the following products:—

(i) *Petroleum ether* or *ligroin* (C_4H_{10} — C_6H_{14}), which is employed as a solvent in the rubber and varnish industries.

(ii) *Petrol or gasoline* (C_6H_{14} — C_8H_{18}), which finds extensive application as a fuel in the motor and aeroplane engines. It is also used for making petrol-air gas, as a solvent, and for dry cleaning.

(iii) *Benzine*, which is used as a solvent, for dry cleaning, and as a substitute for turpentine oil in the preparation of varnishes.

(2) **Kerosene Oil.** This is used as an illuminant and a fuel. It is refined by treatment with concentrated sulphuric acid.

The oil is agitated with the required quantity of the acid (1.5 to 2 per cent) by a blast of cold air in a tall cylindrical tank of iron lined with sheet lead. The agitation is allowed to go on as long as action is indicated by rise of temperature, when the black-coloured, thick acid-tar (consisting of sulpho-compounds of the olefines and other unsaturated hydrocarbons) is allowed to settle and withdrawn through a pipe attached to the bottom of the tank. After the acid treatment, the oil consists of the paraffin hydrocarbons largely freed from olefines and other hydrocarbons. It is washed with water, until the wash-water shows no acid reaction. Then about 1 per cent. of sodium hydroxide solution of 12°Bé is introduced and the mixture agitated. The waste alkali is run off, and the oil is transferred to settling tanks. Here, any water present in the oil settles out, and the oil becomes clear and brilliant.

Kerosenes to be used in lamps should not be sufficiently volatile at the ordinary temperatures to form explosive mixtures with air. The *lowest temperature at which an oil gives off a sufficient amount of vapour to form an explosive mixture with air* is termed its flash point. To protect the public against the low-flash oils, which would be dangerous to use in lamps, laws have been made by different Governments, forbidding the sale of oils having flash points below a certain minimum. The minimum flash-point prescribed differs in different countries. In India, which has a hot climate, it is fixed at 44°C , while in France, which has a colder climate, a minimum flash-point of 35°C is permitted. In Great Britain it is unduly low (22.8°C).

The flash-point of an oil is usually determined by means of Abel's apparatus (Fig. 51). The sample to be tested is placed in a small, metal cup, *A*, which is gradually heated by means of the surrounding water bath, *B*. A small test flame, *F*, is lowered into the space above the oil from time to time by means of an automatic device. As soon as the vapour ignites with a minute explosion the temperature, indicated on the thermometer, T_1 , is noted. Besides this thermometer, which is graduated from 10° to 50°C , there is another T_2 , graduated from 50° to 75°C for the water bath.

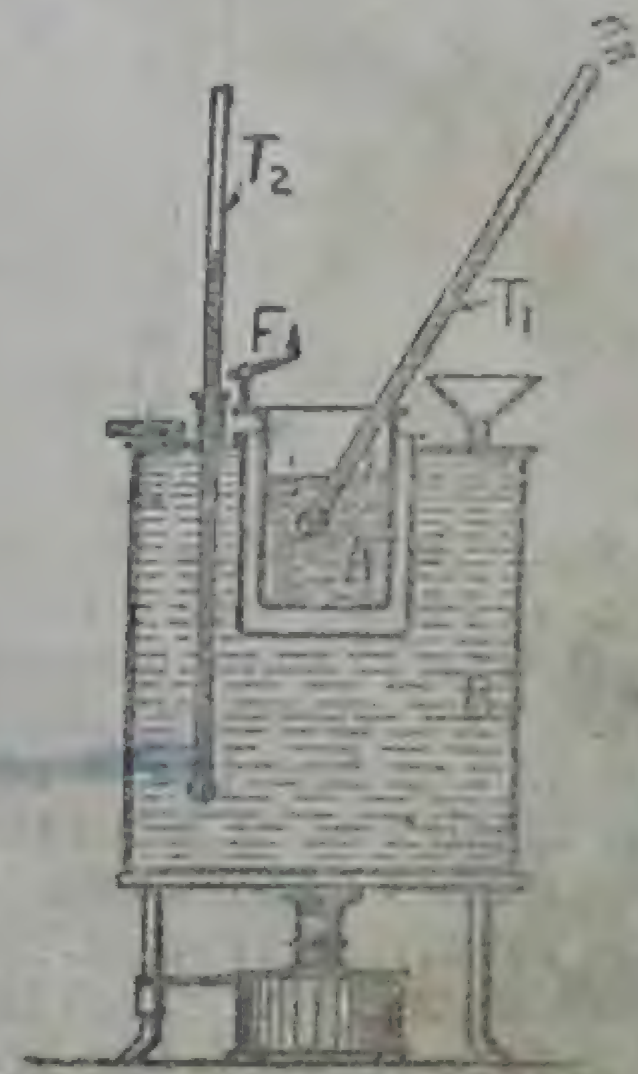


Fig. 51. Abel's Flash-point Apparatus.

Expt. 23. Place some kerosene oil in a beaker provided with a thermometer and heated on a water bath. After every one degree rise of temperature above 30° , test the vapour inside the beaker by means of a lighted match. The temperature at which the vapour ignites with a small explosion is taken as the approximate flash-point of the oil.

(3) **Heavy oil and Paraffin.** This fraction is strongly cooled to separate the solid constituents, which are used as paraffin wax. The liquid portion, from which the wax has been separated, is redistilled in a current of steam, and separated into the following fractions:—

(i) *Fuel Oil or Gas Oil.* This is the first fraction, and is employed as fuel oil in Diesel engines. It is also used for making oil-gas and gasoline by a process of cracking (Secs. 77 and 78).

(ii) *Lubricating Oils.* The fractions that follow gas-oil are used as lubricating oils.

(iii) *Vaseline.* This is the last fraction to pass, and is semi-solid in consistency. It is used in toilet, as a vehicle for ointments, and as a lubricant.

(iv) *Tar.* The dark tarry liquid that is left in the still is periodically drawn off, and is further distilled in cast-iron “coking” stills.

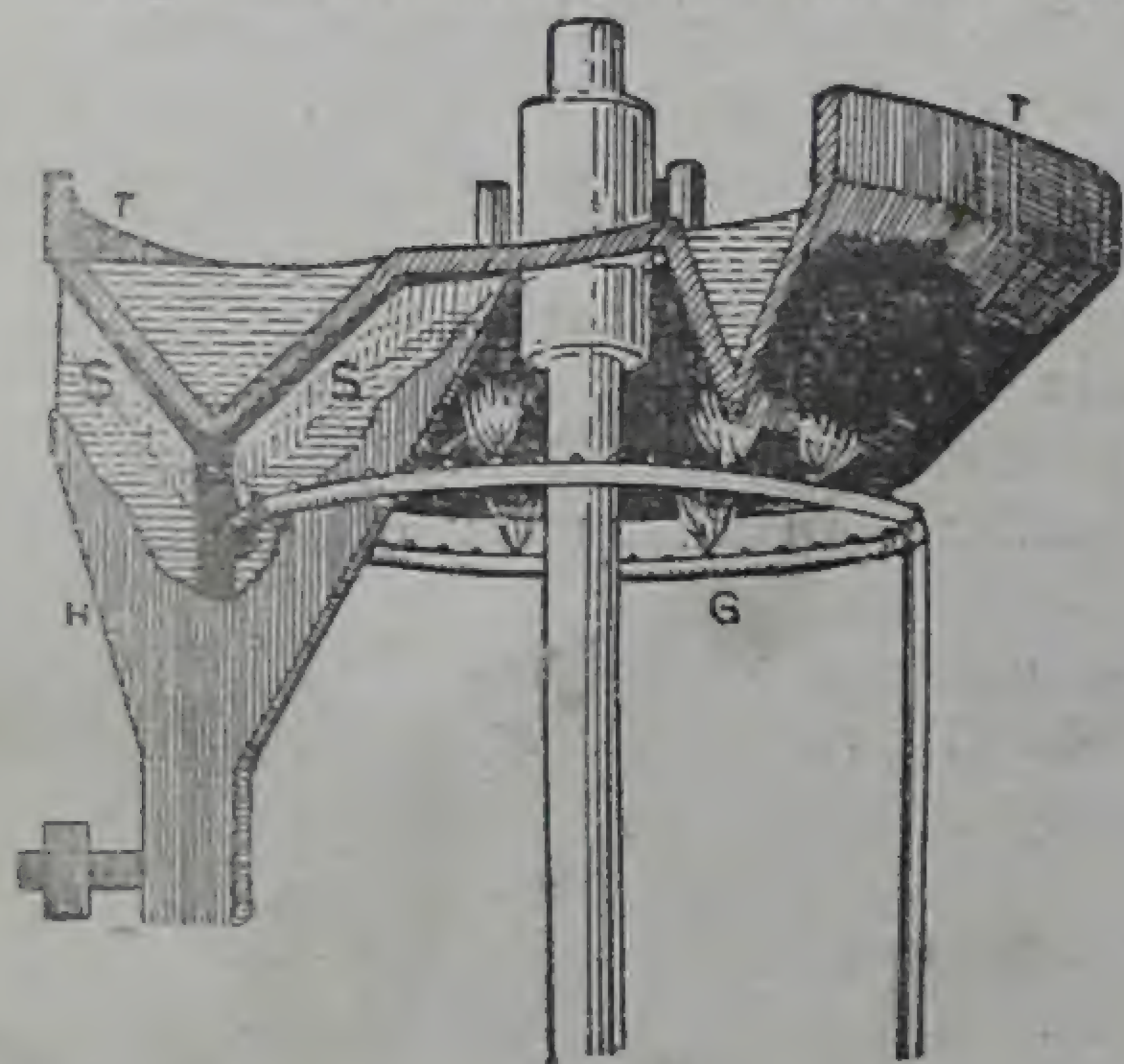


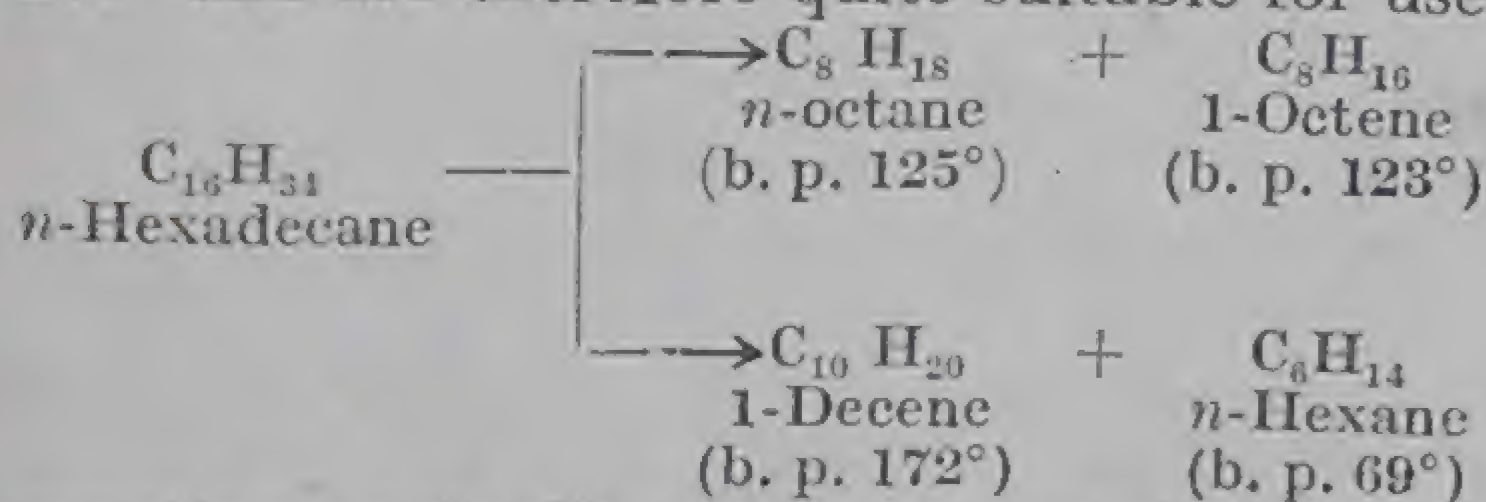
Fig. 52. Apparatus for making Lamp-black. A water-cooled revolving trough of cast iron (*T*) is mounted on a hollow shaft. The circular gas burner, *G*, is fixed up under the trough, and the thick black smoke from the large number of flames deposits on the underside of the revolving trough. The scraper, *S*, continuously removes the lampblack, which falls through the hopper *H* into sacks.

The distillate consists of “heavy oil and paraffin,” and is separated into *paraffin wax*, *lubricating oils* and *vaseline*, as described above. The residue in the still is petroleum coke which is used as a fuel.

(v) *Gas.* The gas that comes off from the last condenser is strongly cooled in order to separate the light-gravity gasoline carried by it. The residual gas was formerly burnt under the stills and in gas-engines. At present, much of it is treated to recover butane and propane. At the ordinary temperature these two gases can be kept in the liquid state under a reasonable pressure. They are, therefore, stored in steel cylinders and are used to supply gas to isolated homes and communities. The gas is also used for making lamp-black. (Fig. 52).

77. Cracking of Petroleum. The term “cracking” is applied to the chemical decomposition of higher hydrocarbons with

the production of lower hydrocarbons. The process is extensively employed in the manufacture of petrol from fuel oils etc. To take a specific example, hexadecane, $C_{16}H_{34}$ (b. p. 288°), is not volatile enough to be used as a motor fuel. On being heated to a dull-red heat, the molecule may undergo a rupture, say near the middle of the carbon chain. The resulting hydrocarbons will then have nearly half the molecular weight of hexadecane. All such hydrocarbons boil below 200° and are therefore quite suitable for use as motor fuel.



The reactions, actually, are very complex, and a large number of hydrocarbons (both gaseous and liquid) are produced by the molecule undergoing rupture in a variety of ways. At the same time, there is a separation of carbon or of hydrocarbons of very high molecular weight, as condensation goes on side by side with the decomposition.

The cracking of heavy oils to get petrol is carried out to a very considerable extent. The economical product of petrol requires that gaseous and high molecular weight by-products be minimized by suitable control of temperature, pressure, the time allowed for cracking and the use of catalysts. There are two types of cracking processes; namely the liquid-phase cracking processes and the vapour phase cracking processes.

The former are used to a much larger extent than the latter. Here the fuel oil is heated under high pressure so as to keep the cracking stock in the liquid state until cracking occurs. Suitable catalysts are added so as to effect the cracking at a much lower temperature and thus to obtain better yields of the volatile liquids. Among many substances used as catalysts in different processes mention may be made of iron, copper, alumina, titanium dioxide and aluminium chloride.

In the vapour-phase processes, the cracking stock is distilled and the vapour are raised to a temperature of about $600^\circ C$. Here the loss in gaseous by-products is increased, but the petrol obtained possesses a higher anti-knock value¹:

¹ In the motor engine where the mixture of petrol vapour and air is highly compressed before ignition, ordinary petrol tends to explode before the piston head reaches the end of its stroke. This premature explosion causes engine knock and therefore loss of power. Anti-knock fuels, which burn smoothly under high compression, are much used in the United States of America. They generally contain a small amount of lead tetraethyl, $Pb.(C_2H_5)_4$, which has a remarkable effect of reducing engine knock.

The unsaturated hydrocarbons present in the products of cracking are readily oxidized in the air and possess an objectionable odour. The cracked gasoline is sometimes hydrogenated in the presence of finely-divided nickel and thus converted into the corresponding saturated hydrocarbons.

78. Oil Gas. In making *oil gas*, a thin stream of oil is allowed to flow into a cast-iron retort heated to dull redness (Fig. 53). The

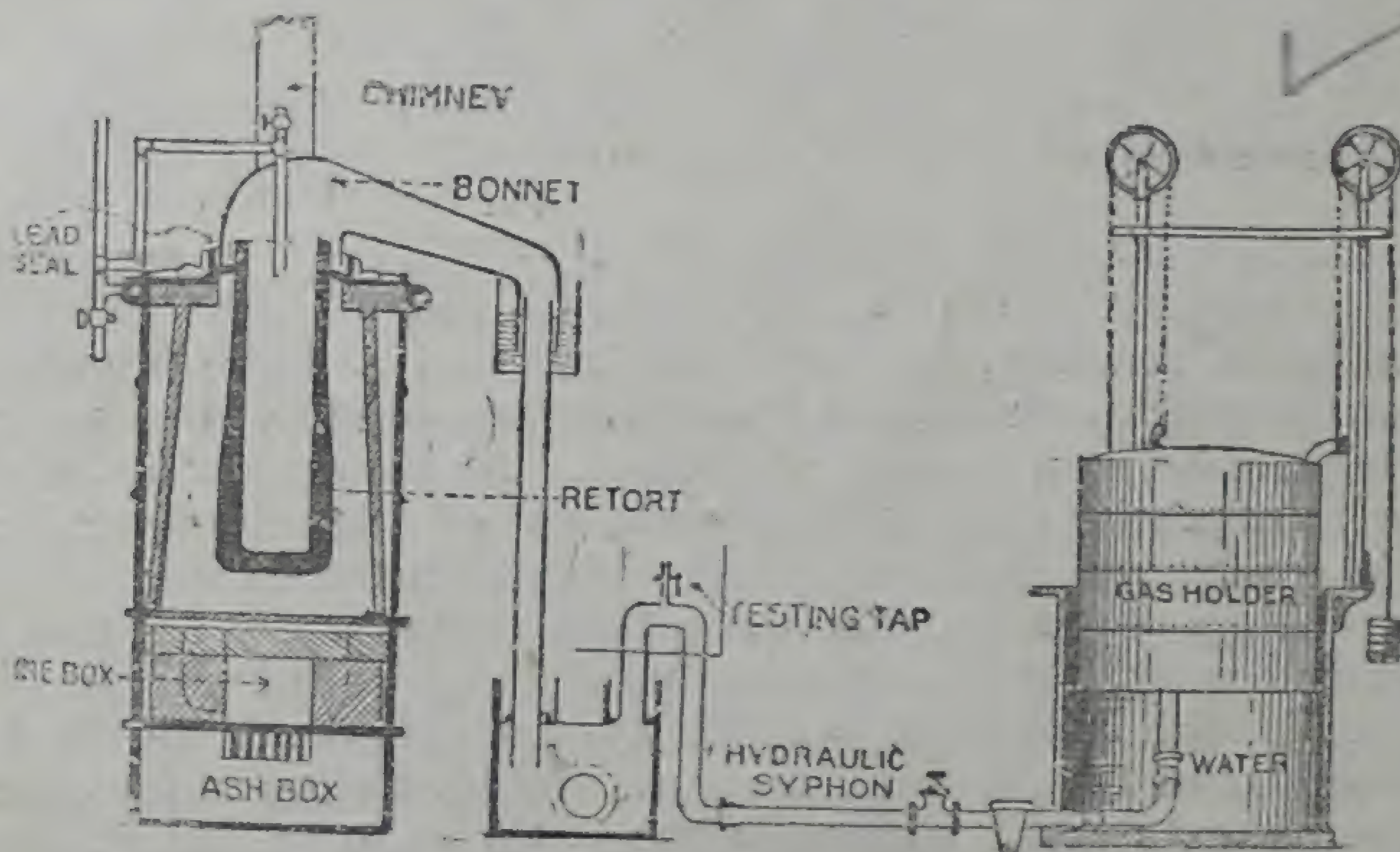
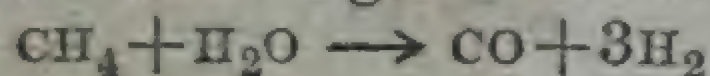


Fig. 53. Oil-Gas Plant.

cracking of the liquid hydrocarbons occurs with production of gaseous hydrocarbons, methane, ethane, ethylene, etc. The gas is first passed through a scrubbing box, which retains the tarry matter present in it, and is then collected in gas-holders.

79. Natural Gas. Natural gas is found usually in association with petroleum deposits. It contains about 85 per cent of methane and about 15 per cent of ethane and other hydrocarbons. It is extensively used in the United States and Canada as a fuel and illuminant in houses, for raising steam in boilers, and making steel, glass and pottery.

A recent use of natural gas is for the manufacture of hydrogen. The Standard Oil Company of New Jersey, U.S.A., have put up a plant capable of producing 300,000 cubic feet of hydrogen per hour. In this process, natural gas is mixed with steam and passed over a catalyst (consisting of iron or cobalt together with aluminium oxide) kept at $1,000^{\circ}\text{C}$, when the following reaction occurs :—



The carbon monoxide is removed from the mixture by oxidation to carbon dioxide and absorption in water as in the Bosch process for the manufacture of hydrogen from water gas.

80. Shale. Bituminous shale, occurring in Scotland, France, and U.S.A. is an important source of liquid and solid paraffins. It is subjected to dry distillation, when ammonia, inflammable gases and shale tar are obtained. The latter, after being washed with concentrated sulphuric acid and caustic soda, is subjected to fractionation to obtain naphtha, burning oil, lubricating oil and paraffin wax.

81. Ozokerite. Ozokerite or Earth wax is often found near the surface of the ground in certain localities. Extensive deposits occur in eastern Galicia. It is a dark-coloured material, consisting of solid paraffin hydrocarbons, and is supposed to have been formed by the evaporation of shallow deposits of petroleum. It is refined by melting out from earthy impurities, and the brownish product, after being treated with concentrated sulphuric acid and alkali, is decolorized with charcoal. The purified material is used as a substitute for beeswax under the name "ceresin."

QUESTIONS

1. Describe the general methods of preparation of the hydrocarbons of the paraffin series. Name six compounds of this series and give their structural formulæ. (Punjab, Inter., 1934)
2. Give an account of the physical and chemical characters of the paraffin hydrocarbons. What is the general molecular formula assigned to this series?
3. Give an account of the occurrence of methane. How will you prepare a sample of this hydrocarbon in the laboratory and what experiments will you perform to illustrate its important properties? "Methane is a saturated hydrocarbon." Explain this statement.
4. Describe the various methods by which methane has been synthesized. How will you distinguish between methane and another hydrocarbon of this series?
5. Give the various methods for the preparation of ethane. How may a pure sample of the gas be prepared in the laboratory?
6. How has the constitutional formula of ethane been arrived at? Give as many facts as you can in support of the formula you deduce.
7. Write a note on the nomenclature of isomeric paraffins. Write the structural formulæ of the following hydrocarbons: *Neopentane*, *dimethylethyl methane*, *1-methyl-5-isopropyl-hexane*.
8. Describe the occurrence, composition, and probable origin of natural petroleum. Give an outline, in brief, of the method of treatment of the crude product and indicate the main applications of the derived materials. (Punjab, B.Sc., 1942)
9. What do you understand by the term *flash point*? How is it determined and what is its importance?
10. Write a note on *cracking of oils*. Explain the use of *anti-knock fuel* for motor engines.
11. Write notes on (a) natural gas, (b) Wurtz' synthesis. (c) Kolbe's reaction, (d) Origin of petroleum.

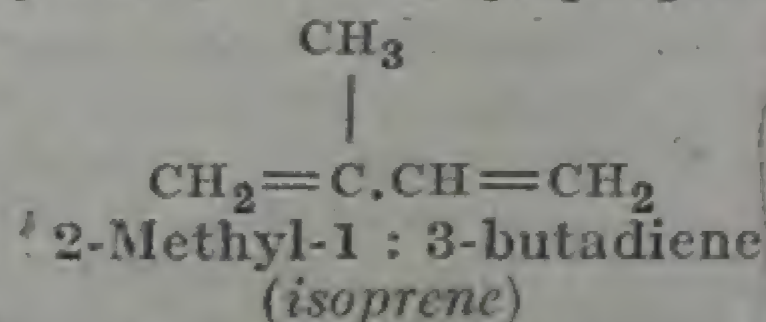
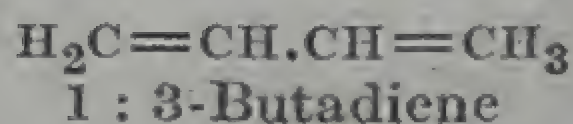
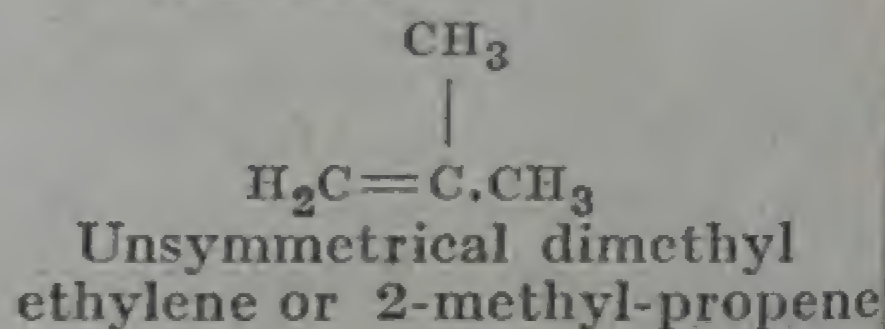
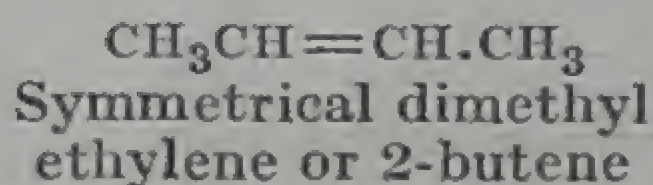
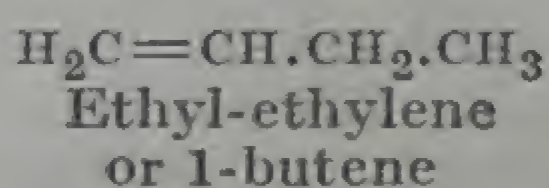
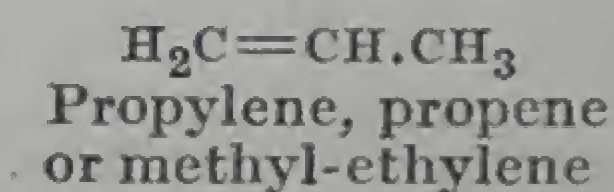
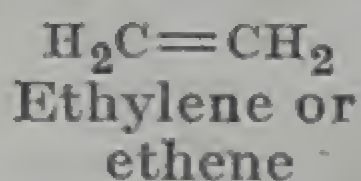
CHAPTER XI

UNSATURATED HYDROCARBONS

82. General Formulæ and Nomenclature. There are two main series of unsaturated aliphatic hydrocarbons—the olefines and the acetylenes. The former contain a double and the latter a triple bond. The general formula for the olefines is C_nH_{2n} and that for the acetylenes C_nH_{2n-2} .

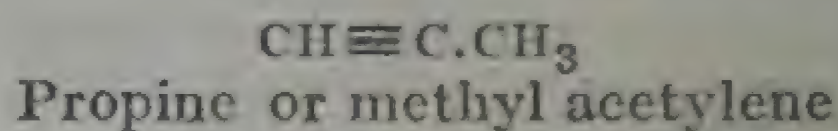
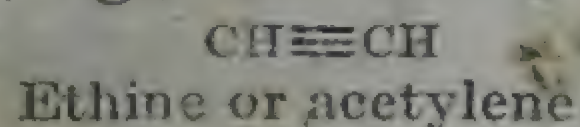
In addition to these, hydrocarbons containing two double bonds or two triple bonds are known. They are called diolefines and diacetylenes respectively. The general molecular formula for diolefines is the same as for acetylenes, *viz.*, C_nH_{2n-2} , and for the diacetylenes, it is C_nH_{2n-6} .

The olefines are named after the corresponding paraffins by changing the termination *-ane* into *-ylene*, or according to the Geneva system, into *-ene*; in the case of diolefines the ending *-diene* is used. The position of a double bond is indicated by adding the letter or number of the *first* atom of the doubly-bound pair of carbon atoms; *e.g.*,



Sometimes, the double bond is indicated by the Greek letter Δ . Thus, unsymmetrical dimethyl ethylene is called 2-methyl- Δ -1-propene.

The acetylene hydrocarbons are named in a similar manner to olefines, the termination *-ine* or *diene* being used instead of *-ene* or *-diene*; *e.g.*,



$\text{CH}\equiv\text{C}\cdot\text{CH}_2\cdot\text{CH}_3$
1-Butine or ethyl acetylene

$\text{CH}_3\text{C}\equiv\text{C}\cdot\text{CH}_3$
2-Butine or dimethyl acetylene

$\text{CH}\equiv\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\text{C}\equiv\text{CH}$
1 : 5-Hexadiene or dipropargyl

OLEFINES OR HYDROCARBONS OF ETHYLENE SERIES

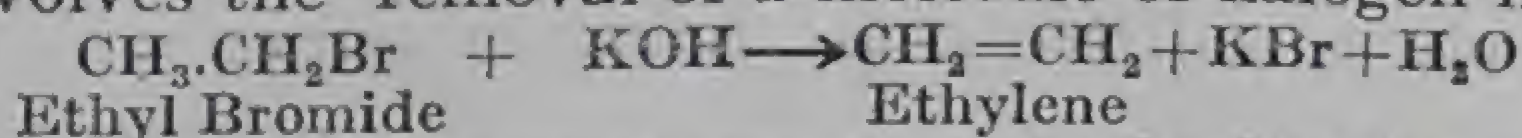
83. General Methods of Formation :

(1) From *alcohols*, by dehydration by means of hot, concentrated sulphuric acid, phosphoric acid, or zinc chloride ; *e.g.*,



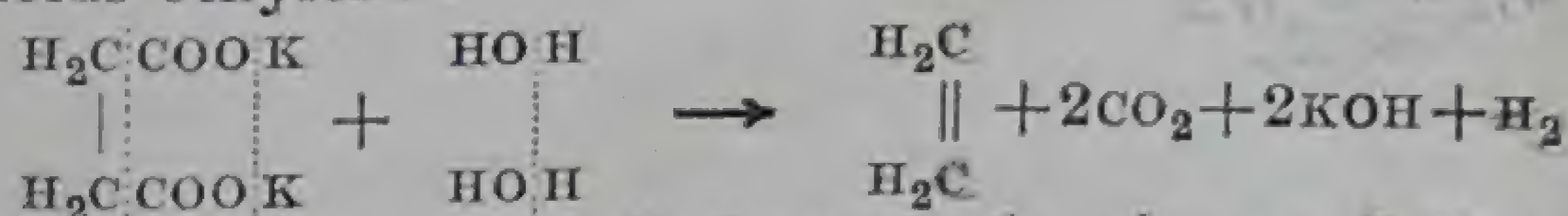
An alternative method consists in passing the alcohol vapour over heated alumina (*catalytic dehydration*, Sec. 65). Secondary and tertiary alcohols lose the elements of water more readily than primary alcohols.

(2) From *alkyl halides*, by heating with alcoholic potash ; the reaction involves the removal of a molecule of halogen hydride :



Sabatier and Mailhe have shown that finely-divided nickel, copper or cobalt can bring about the catalytic decomposition of alkyl halides into olefines and halogen hydrides.

(3) From the dibasic acids of the succinic acid series, by electrolysis of a concentrated solution of potassium salts ; thus succinic acid itself yields ethylene :



The complex anion, when discharged, breaks up into ethylene and carbon dioxide.

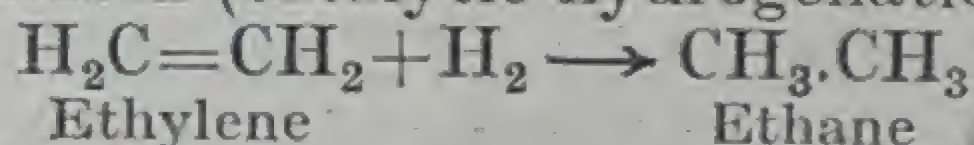
(4) Olefines are produced, together with paraffins, by the destructive distillation of many substances, such as wood, lignite and coal. They are also formed by the "cracking" of higher paraffins. The presence of ethylene in coal-gas and oil-gas is due to these causes.

84. Physical Properties. As in the case of the methane series, ethylene hydrocarbons show a gradual change in their physical properties. The lower members, up to C_6H_{10} , are gases, the following fourteen or so are liquids, while the higher ones are solids. The boiling-points of the corresponding hydrocarbons of the methane and the ethylene series lie very close together, but the melting-points of the olefines are somewhat lower than those of the paraffins. Olefines are readily soluble in alcohol, but practically insoluble in water.

85. Chemical Properties. Olefines are *unsaturated* hydrocarbons, and their most characteristic property is that of *addition*

(Sec. 36). The double bond that their molecules contain is capable of taking up two monovalent atoms or groups, getting converted into a single bond, with the formation of saturated compounds. The most important addition reactions of olefines are :

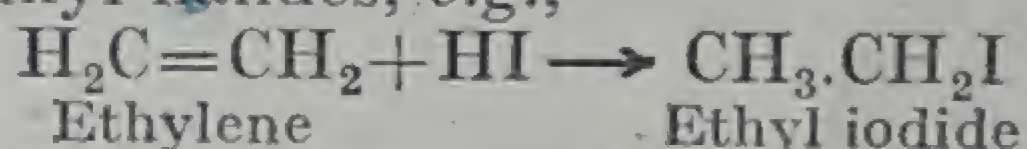
(1) In the presence of finely-divided nickel, they combine with hydrogen, yielding a paraffin (catalytic hydrogenation, Sec. 65) *e.g.*,



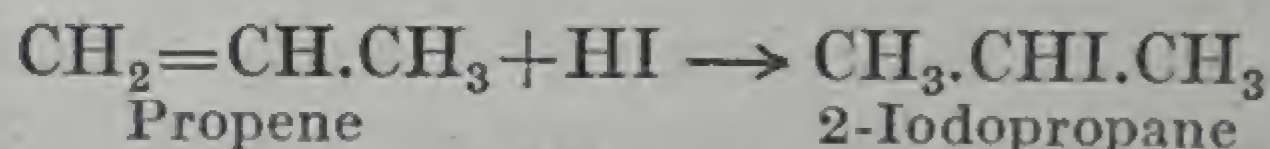
(2) They combine with chlorine, bromine and iodine, forming dihalogen derivatives ; *e.g.*,



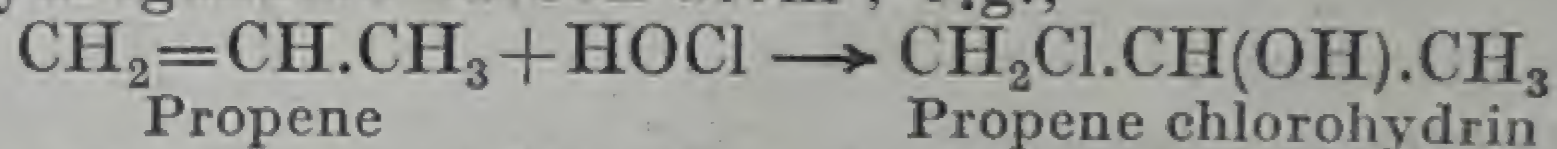
(3) They also combine with halogen hydrides (of which HI is most reactive), yielding alkyl halides, *e.g.*,



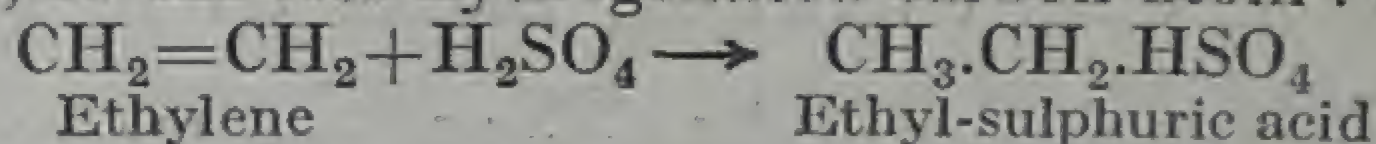
According to Markownikoff's rule, the negative constituent goes to that carbon atom which carries the *smaller* number of hydrogen atoms ; *e.g.*,



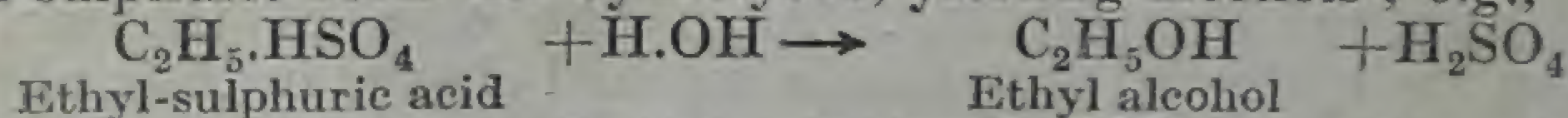
(4) Combination with hypochlorous acid, HOCl^1 , gives rise to chlorohydrins. In this case, the electronegative *hydroxyl* group goes to the less hydrogenated carbon atom ; *e.g.*,



(5) Olefines are absorbed by concentrated sulphuric acid, forming alkyl-sulphuric acids, the electronegative group— HSO_4 , attaching itself, as usual, to the less hydrogenated carbon atom : *e.g.*,

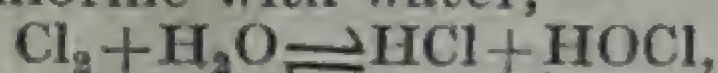


On diluting with water and boiling the resulting aqueous solution, the alkyl-sulphuric acids are hydrolysed, yielding alcohols ; *e.g.*,

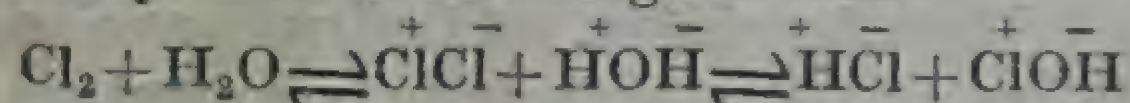


It is thus possible to effect the indirect addition of the elements of water to an olefine, with the production of an alcohol.

¹ According to W. A. Noyes, the halogens possess an amphoteric character. The reversible reaction of chlorine with water,

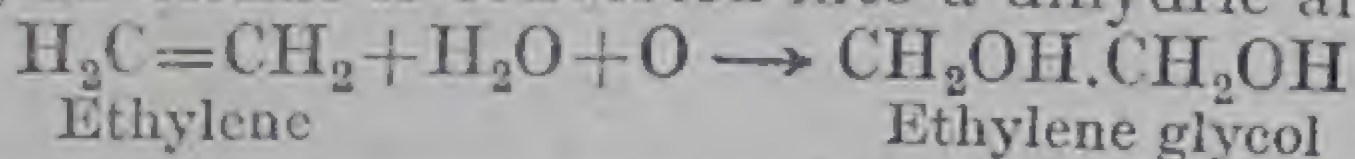


is formulated most readily as an interchange of ions :—

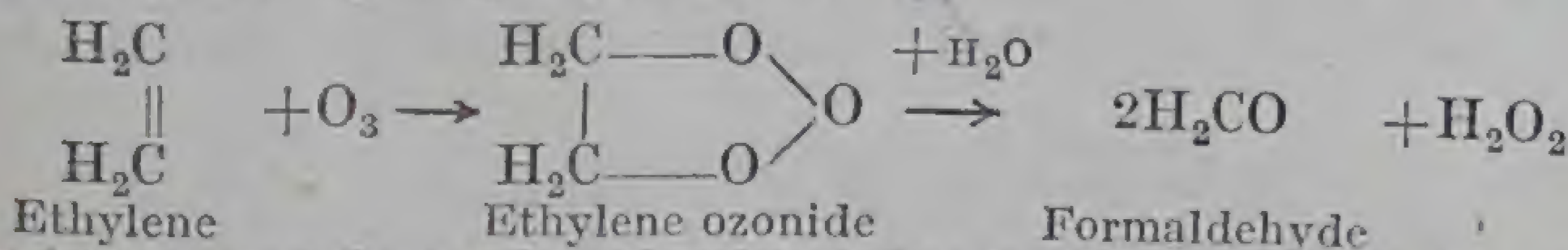


The addition of sulphuric acid occurs much more readily in the case of higher olefines than with ethylene; thus, while ethylene requires fuming sulphuric acid, propylene is absorbed by 85 per cent sulphuric acid. In the case of many of the more complicated members, addition of the acid and the hydrolysis of the product-formed proceed under the same conditions, so that shaking the olefines with dilute sulphuric acid (even 10 or 20 per cent.) transforms them into the alcohols.

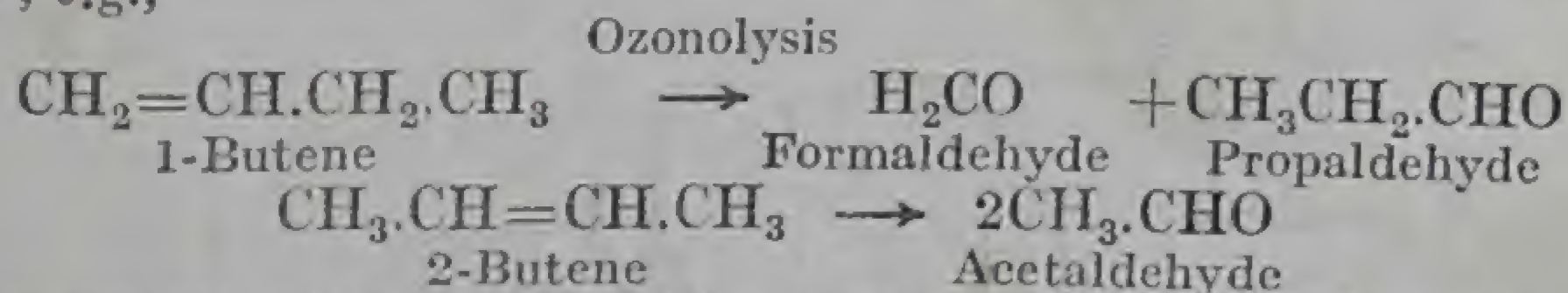
(6) When treated with a cold, dilute, alkaline solution of potassium permanganate, an olefine is converted into a dihydric alcohol;



(7) Olefines and other compounds containing double bonds react with ozone, yielding explosive compounds, called ozonides. These contain a molecule of ozone attached to each double bond, and on being warmed with water or dilute acid, they are decomposed into aldehydes or ketones, and hydrogen peroxide.



By determining the number of carbon atoms in the molecule of the aldehyde or ketone thus produced, the *position* of the double bond in the compound is revealed; e.g.,



The above method of "ozonolysis" has been used for elucidating the constitution of complex olefinic substances including rubber.

86. Detection of Double Bond. The presence of a double bond in a compound can be detected by the following methods:

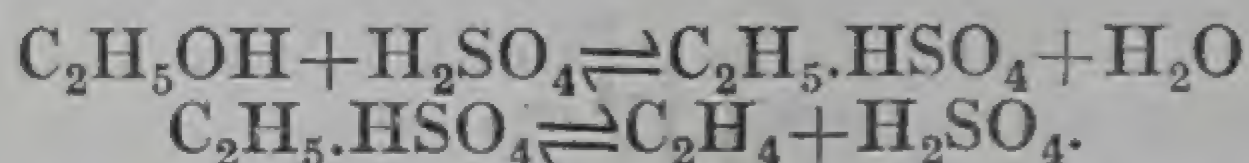
- (1) Decolorization of a cold, dilute, alkaline solution of potassium permanganate (Baeyer's reagent).
- (2) Decolorization of bromine water.
- (3) Physically, by the determination of parachor (Sec. 44) which undergoes a specific increment through the presence, in the molecule, of a double bond.

87 Ethylene, *Ethene*, $\text{H}_2\text{C}=\text{CH}_2$.

Occurrence. Ethylene occurs to the extent of about 5 per cent in coal gas and in the gas from the coking ovens. It is also present in wood-gas.

Preparation. Ethylene may be obtained by any of the general methods already described (Sec. 83). In the laboratory, it is usually

obtained by heating a mixture of ethyl alcohol and concentrated sulphuric acid to about 160°C . The reaction has been shown to take place really in two stages. In the first instance, ethyl hydrogen sulphate, $\text{C}_2\text{H}_5\cdot\text{HSO}_4$, is produced; this then decomposes to give ethylene and water :—



Expt. 24. A mixture of 30 c.c. of alcohol and 75 c.c. of concentrated sulphuric acid together with enough sand to form a thin paste is placed in a large size, round-bottom flask provided with a delivery tube and a dropping funnel (Fig. 54). The stem of the latter should be drawn out to a fine point and slightly bent, so that it could be kept filled with liquid and thus prevent the escape of the gas through it. The object of adding sand to the mixture in the flask is to prevent frothing. The flask is heated on a sand bath, until a steady stream of gas is evolved ($160\text{--}165^{\circ}\text{C}$). When the evolution of gas becomes slow, a further supply may be obtained by dropping a mixture of equal volumes of alcohol and concentrated sulphuric acid. The evolved ethylene is contaminated with alcohol and ether vapours, carbon dioxide and sulphur dioxide. It is, therefore, passed

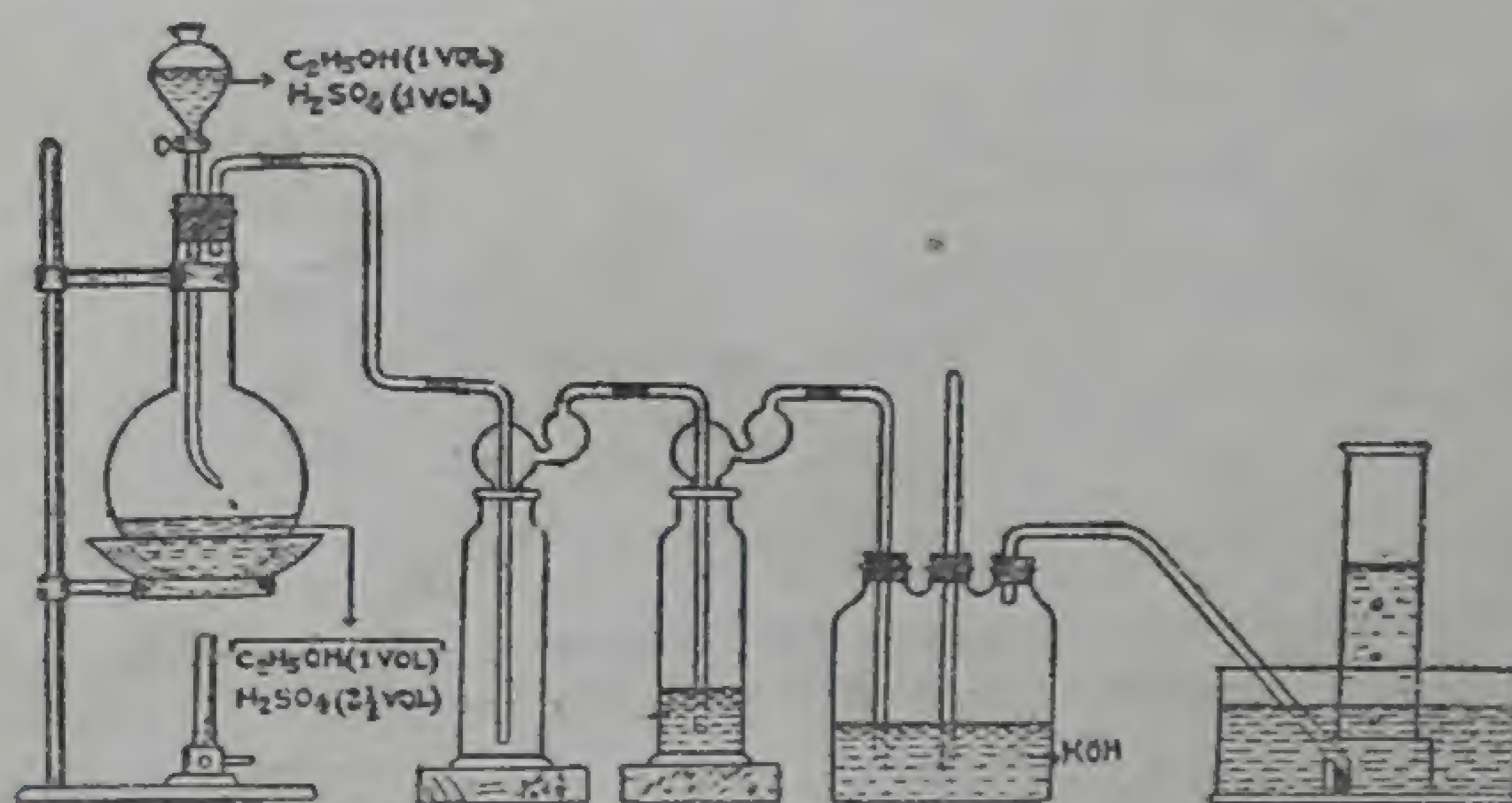


Fig. 54. Preparation of Ethylene.

first through a cold empty wash-bottle, in order to condense alcohol and ether vapours, then through one or more wash-bottles containing a solution of potassium hydroxide to remove CO_2 and SO_2 . The gas thus purified is collected over water in glass cylinders.

An alternative method of preparing ethylene, free from carbon dioxide and sulphur dioxide, consists in dropping ethyl alcohol into syrupy phosphoric acid heated to about 220° . As the reaction is continuous, an almost unlimited amount of the alcohol can be decomposed by a relatively small amount of phosphoric acid.

Expt. 25. About 50 c.c. of syrupy phosphoric acid (sp. gr. 1.75) are placed in a 250 c.c. distillation flask provided with a dropping funnel (the stem of which is drawn out to a fine point reaching to the bottom of the flask) and a thermometer (the bulb of which dips in the acid). The flask is heated on a sand bath, until the temperature rises to 220° , and then a quantity of alcohol is run

very slowly. The evolved gas is passed through a wash bottle surrounded by ice in order to condense water, alcohol, and ether vapours, and is then collected over water.

Manufacture. Ethylene is prepared on a large scale by three different methods :

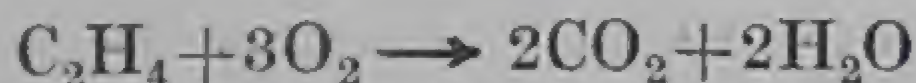
(1) By passing alcohol vapour through a heated tower filled with coke moistened with syrupy phosphoric acid.

(2) By passing alcohol vapour through heated tubes containing kaolin.

(3) In the natural gas region, by cracking propane by passing it through heated tubes.

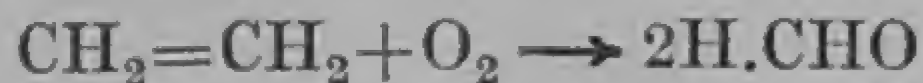
Physical Properties. Ethylene is a colourless gas having a faint ethereal odour. It is sparingly soluble in water, but fairly so in alcohol and ether.

Chemical Properties. (1) Ethylene burns with a luminous flame, and, like other hydrocarbons, forms an explosive mixture with air or oxygen.



(2) It shows the various addition reactions, described under Sec. 85.

(3) Willstatter and Bommer have found that the oxidation of ethylene by means of atmospheric oxygen yields a fairly good yield of formaldehyde :



Expt. 26. (a) Ignite a cylinder of ethylene. Notice that it burns with a bright flame.

(b) Invert a jar containing ethylene over another containing chlorine. Notice that the colour of chlorine soon disappears, with the simultaneous production of oily drops of ethylene chloride.

(c) Repeat the above experiment, using bromine vapour instead of chlorine.

(d) Pour some bromine water into a jar of ethylene and shake. Notice that the colour of bromine disappears.

(e) Repeat the above experiment with a dilute, acidified solution of potassium permanganate.

Constitution. See Sec. 37.

Uses. (1) Considerable quantities of ethyl alcohol are now made in the U.S.A. from ethylene obtained (together with other gases) by "cracking" petroleum or natural gas.

(2) Ethylene is now being used instead of acetylene for *cutting* and *welding*. Though inferior to acetylene so far as the flame temperature goes, it has a distinct advantage over the latter in that it can be stored and transported in cylinders under high pressures without danger of explosion.

(3) It is also finding an extensive use in the fruit industry. Fruit is gathered and transported before it is fully ripe. On its arrival, it is kept for a few days in an atmosphere containing a small proportion of ethylene, which rapidly develops the colour and completes the ripening.

(4) In recent years, ethylene has come into large use as an anæsthetic in place of ether.

(5) Large quantities of ethylene are used in the preparation of *ethylene chlorohydrin*, *ethylene chloride*, and during war days, of *mustard gas*.

Ethylene is likely to find a much wider field of usefulness in the near future. In view of an almost unlimited use of formaldehyde, reaction (3), given above, may prove of considerable individual importance.

88. Higher Homologues.

Propylene (*propene*), $\text{CH}_3\cdot\text{CH}=\text{CH}_2$, is obtained as a by-product in the cracking of heavy oils (Sec. 77). It is employed in the manufacture of isopropyl alcohol.

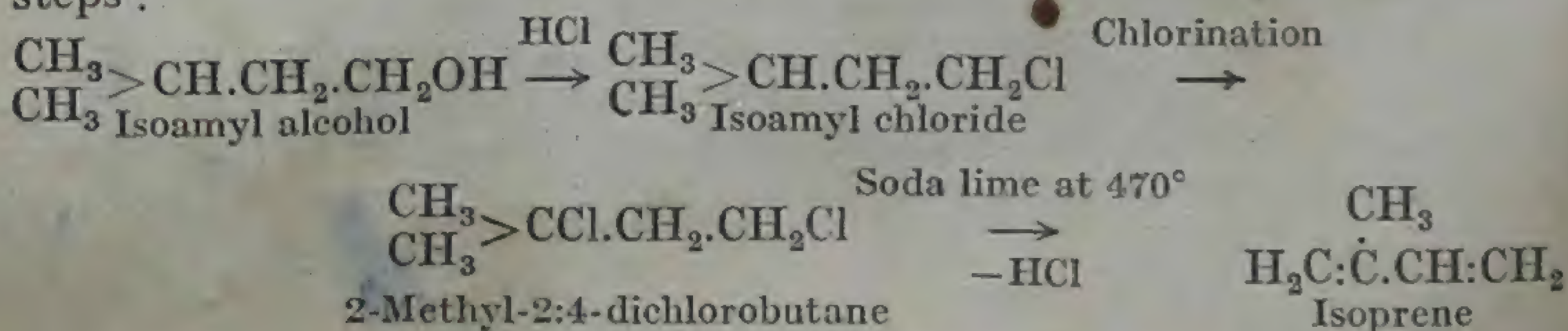
Three butylenes, C_4H_8 , are theoretically possible. All of these are known, but are of little importance. Of the four isomeric pentylenes, C_5H_{10} , one only viz., **Trimethyl-ethylene**, $(\text{CH}_3)_2\text{C}=\text{CH}\cdot\text{CH}_3$, is important. It is commercially obtained from isoamyl alcohol (*q.v.*) by heating the latter to 290° . It is used, under the name of **pental**, as a narcotic of short duration.

DIOLEFINES

89. Diolefines, The diolefines contain two double bonds and have the general formula $\text{C}_n\text{H}_{2n-2}$. In chemical behaviour the hydrocarbons of this series resemble olefines, and combine with *four* monovalent atoms or groups. They differ from the acetylenes (with which they are isomeric) in forming no copper or silver derivatives. On the other hand, they give precipitates with a solution of mercuric chloride.

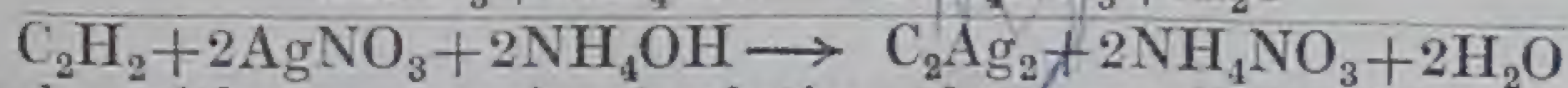
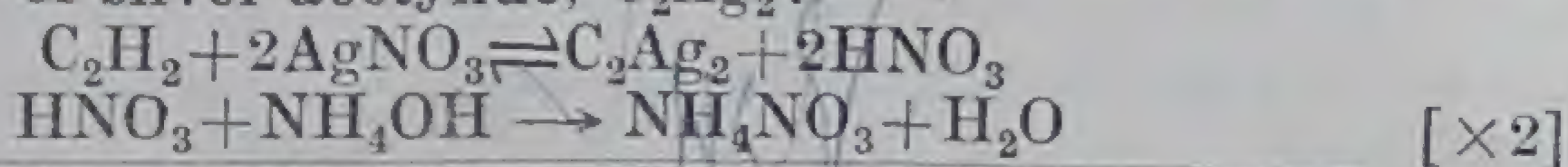


90. Isoprene, $\text{H}_2\text{C}:\dot{\text{C}}\cdot\text{CH}:\text{CH}_2$, or *2-methyl-1-3-butadiene*, because of its close relation to caoutchouc and terpenes, is the most important of the diolefines. It is produced (together with trimethyl ethylene and dipentene) by the dry distillation of caoutchouc, but the yield is very poor (about 2 per cent). On a commercial scale, isoprene may be obtained from the isoamyl alcohol in fused oil in the following three steps:



The polymerization of the acetylene hydrocarbons is an important method of passing from the aliphatic to the aromatic compounds.

(3) **Formation of Metallic Derivatives.** A very characteristic property of acetylene and its *mono*-alkyl derivatives, $R.C\equiv CH$, is the power of forming precipitates with ammoniacal solutions of silver nitrate and cuprous chloride. Thus, when acetylene is passed through an ammoniacal solution of silver nitrate, it produces a white precipitate of silver acetylide, C_2Ag_2 :—



Similarly, with an ammoniacal solution of cuprous chloride a brownish-red precipitate of cuprous acetylide, C_2Cu_2 , is produced. Both these compounds are explosive, silver acetylide being more so than the cuprous compound.

The formation of these precipitates is used as a distinctive test for acetylene and its monoalkyl derivatives, and serves to distinguish these hydrocarbons from all others. Further, since these acetylides are decomposed by acids with regeneration of the acetylene hydrocarbons, their formation is also utilized for the separation of these hydrocarbons from a mixture.

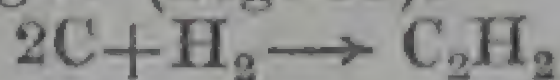
When acetylene or one of its monoalkyl derivatives is passed over heated sodium or potassium, hydrogen is set free, and metallic substitution products, such as C_2HNa and C_2Na_2 , are formed.

The dialkyl acetylenes do *not* form metallic derivatives of the above type, since they contain hydrogen in direct combination with the triply bound carbon atoms.

93. Acetylene, *Ethine*, $CH\equiv CH$.

Occurrence. Acetylene occurs in coal-gas to the extent of about 0.06 per cent. When a Bunsen burner strikes back, the gases formed contain up to 0.8 per cent of acetylene. (See Expt. 28).

Synthesis. Acetylene was first synthesized by Berthelot in 1859 by sparking carbon electrodes in a current of hydrogen (Fig. 55).



Preparation. (1) Acetylene may be obtained from ethylene dibromide (see Sec. 91).

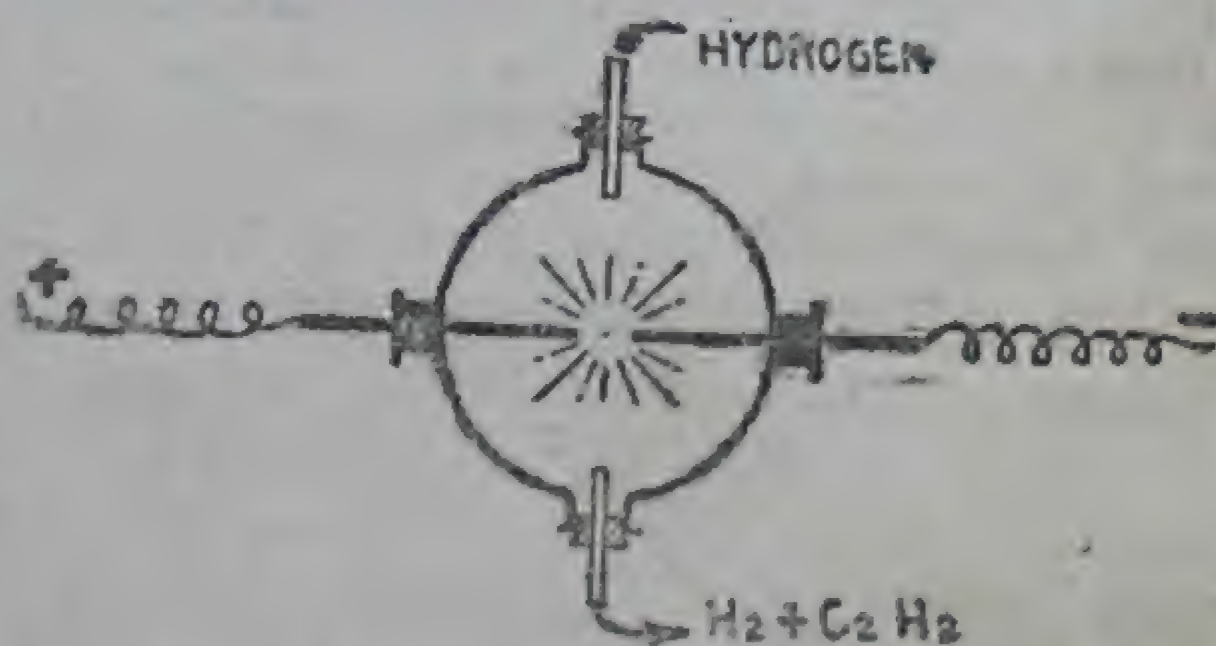
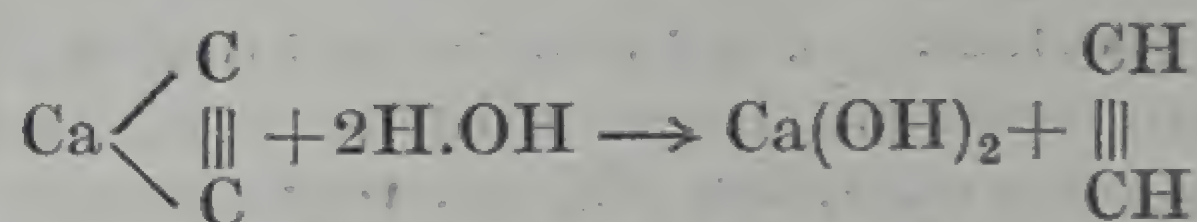


Fig. 55. Synthesis of Acetylene.

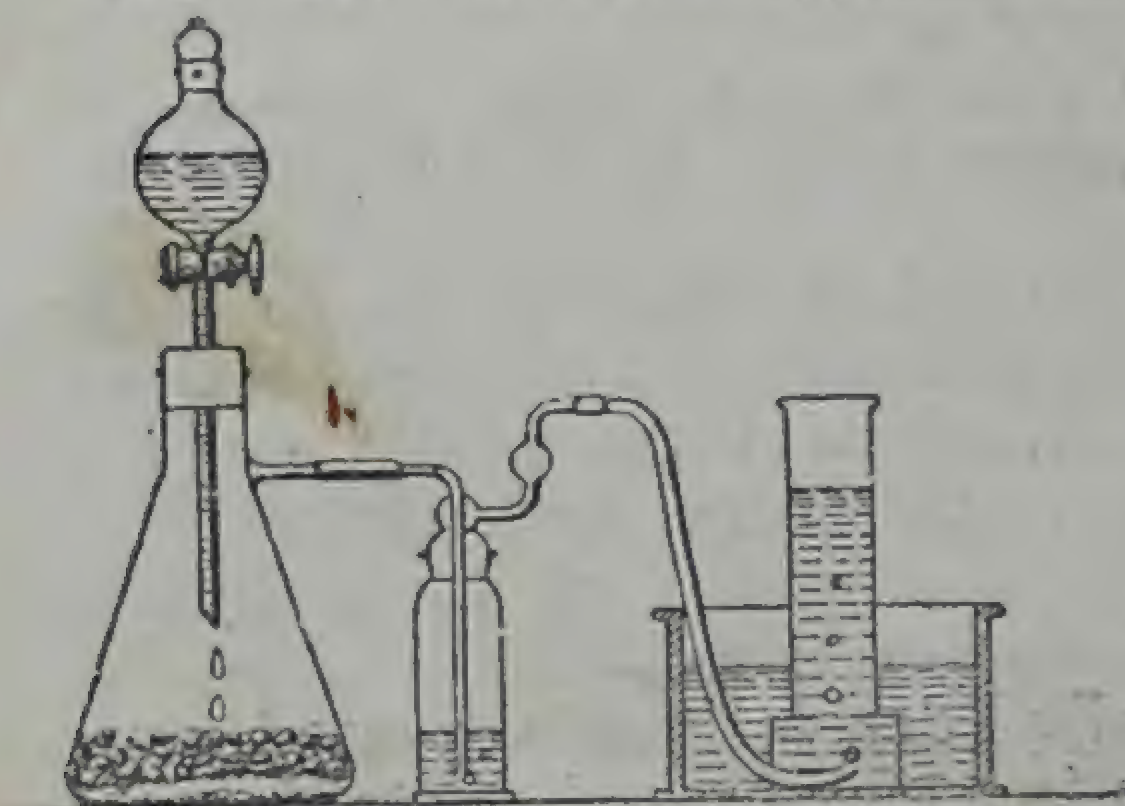
(2) It may also be obtained from acetaldehyde (see Sec. 91).

(3) It is most readily prepared by dropping water on calcium carbide¹;



The gas evolved from the commercial carbide is contaminated with ammonia, hydrogen sulphide and phosphine. It may be washed with an *acid* solution of cupric sulphate, which removes all the above impurities.

Expt. 27. Fit up the apparatus shown in Fig. 56. Place a layer of sand in the filtering flask, and cover this with a few pieces of calcium carbide. Place a solution of cupric sulphate acidified with hydrochloric acid in the Drechsel bottle. Admit water slowly through the dropping funnel, and collect the evolved gas over water.



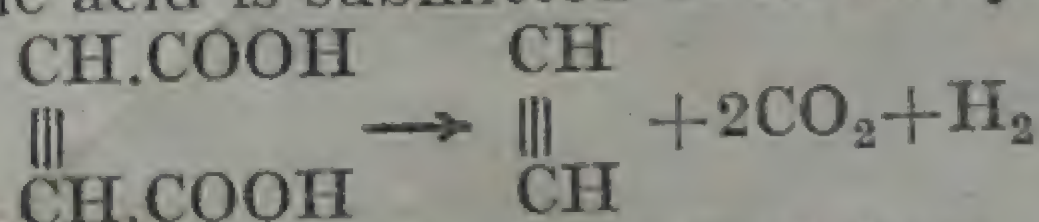
(4) The formation of acetylene during incomplete combustion of coal gas or ether may be shown by means of the following experiments :

Expt 28. Light a Bunsen burner

Fig. 56. Preparation of Acetylene. at the base, and aspirate the resulting gases through a Drechsel bottle containing some ammoniacal cuprous chloride solution. It will be observed that a reddish-brown precipitate of cuprous acetylide is formed (Fig. 57).

Expt. 29. Pour some ammoniacal solution of cuprous chloride into a wide-boiling-tube, and then a little ether. Light the ether at the mouth of the tube, and while it is burning hold the tube in a slanting position and give it a slow rotatory motion. It will be observed that a precipitate of cuprous acetylide is formed in this case also.

(5) Acetylene is also formed when a solution of the sodium or potassium salt of fumaric or maleic acid is submitted to electrolysis :



Purification. The acetylene obtained from commercial calcium carbide contains compounds of phosphorus, sulphur, arsenic and



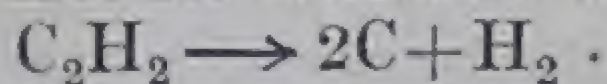
Fig. 57.

¹ This reaction proves that calcium carbide possesses the structure of a true acetylide.

other impurities. The gas is purified by washing with solutions of sodium hypochlorite, lead acetate, potassium dichromate and similar reagents.

Properties. *Physical.* Acetylene is a colourless gas, which when pure, has a peculiar ethereal smell. The objectionable odour of the gas prepared from the commercial carbide is due to impurities, especially phosphine. Water dissolves about 1 volume, alcohol 6 volumes, and acetone 25 volumes of the gas under the ordinary conditions.

Chemical. (1) Acetylene is an endothermic and unstable compound. When submitted to a pressure of more than 2 atmospheres and detonated, it decomposes into its elements with explosive violence :



For industrial purposes, the gas is stored by forcing it into cylinders packed with briquettes soaked in acetone, which absorbs 25×12 or 300 vols. of the gas at 15° and under a pressure of 12 atmospheres.

(2) Acetylene burns with a luminous, smoky flame. When used as an illuminant, it is burnt in special burners, in which the gas sucks in large amounts of air as it issues from two small openings, and burns with a brilliant white flame, which does not emit smoke.

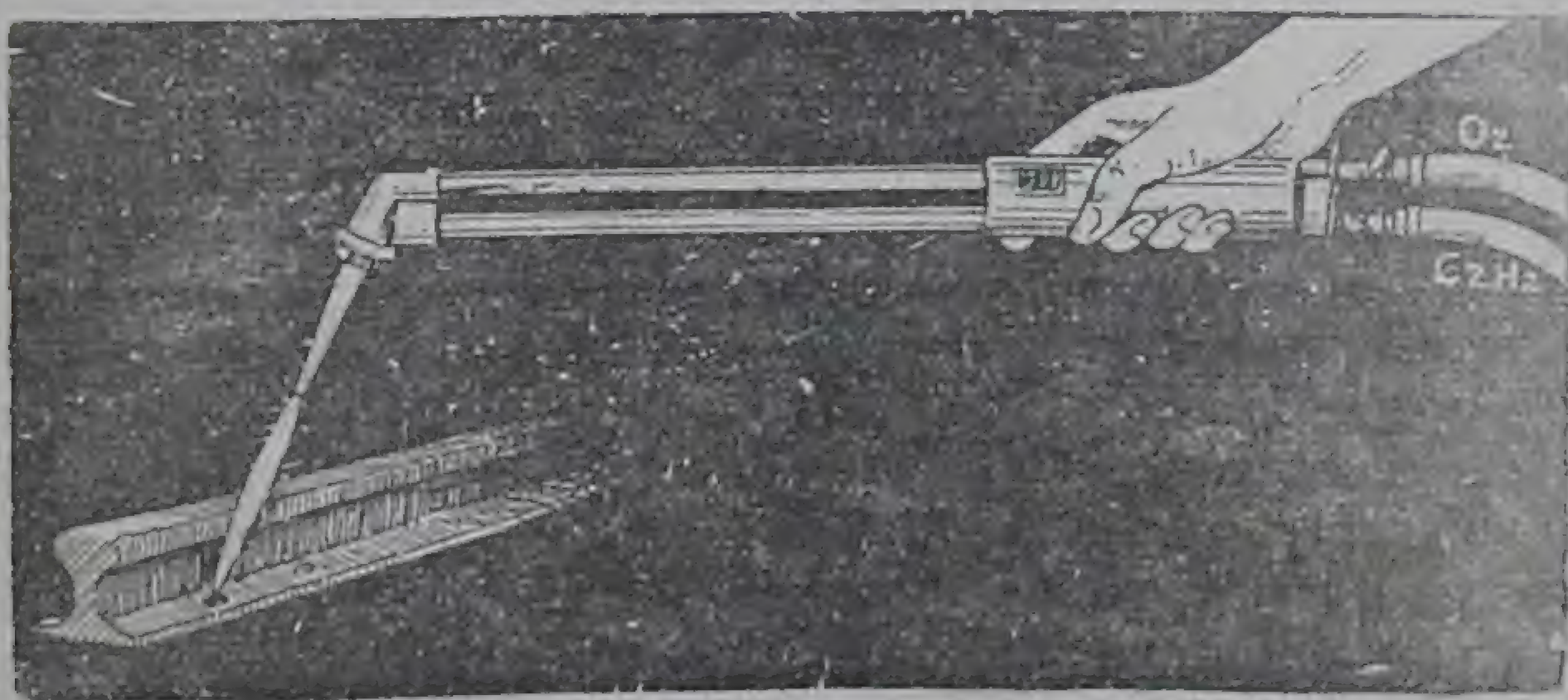


Fig. 58. Oxy-acetylene Torch.

The oxy-acetylene blow-pipe (Fig. 58) gives the hottest of all flames (temp. = $2,700^\circ$), and is used for welding, cutting and making holes into steel plates.

Like all hydrocarbons, acetylene forms an explosive mixture with air.

Expt. 30. Light some acetylene contained in a gas-cylinder : it burns with a smoky flame.

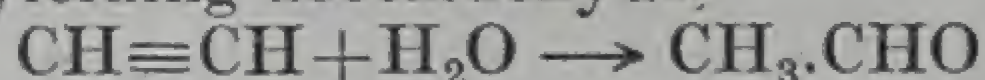
Light the gas in an acetylene burner. Notice that the flame is of dazzling brilliancy.

Acetylene bursts into flame in contact with chlorine, producing free carbon and hydrochloric acid.



However, in the presence of suitable catalysts addition products are formed as usual.

(3) Acetylene shows all the characteristic reactions of the hydrocarbons of this series (Sec. 92). When it is passed into warm, 20 per cent sulphuric acid, containing a little mercuric sulphate, it adds on a molecule of water, yielding acetaldehyde.



This reaction is of considerable commercial importance.

Expt. 31. (a) Place a cylinder containing acetylene over another containing chlorine. Notice that the mixture ignites *spontaneously*, with the deposition of carbon and formation of fumes of hydrogen chloride.

(b) Throw a small piece of calcium carbide into a trough containing water, and bring the end of the delivery tube of a chlorine generator near the bubbles of acetylene as they rise from water; notice that the bubbles of the gas ignite spontaneously.

(c) Pour some ammoniacal silver nitrate solution into a cylinder full of acetylene. Notice that a white precipitate of silver acetylide is formed.

(d) Pour some ammoniacal cuprous chloride solution into another cylinder of acetylene. Notice the formation of a reddish-brown precipitate of cuprous acetylide.

Uses. (1) As already mentioned, acetylene is used as an illuminant and in the oxy-acetylene torch.

(2) Acetylene, carefully purified from all impurities, is used as an anæsthetic under the name Narcylen.

(3) Acetylene is a *synthetic agent* of great importance. It can be readily obtained from its elements, and is very reactive. These two facts make acetylene almost indispensable in a large number of "complete syntheses" of organic substances. The advent of cheap electric energy, derived mainly from water-power, has made it possible to produce calcium carbide, and therefore acetylene, very cheaply. Hence, the possibilities of utilizing acetylene for the manufacture of organic substances of economic value have recently attracted much attention.

The most important synthetic uses of acetylene are :

(a) Conversion of acetylene into *acetaldehyde* (Sec. 93), which in turn yields—

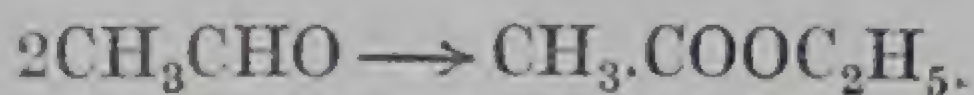
(i) *ethyl alcohol*, by reduction,



(ii) *acetic acid*, by oxidation,



(iii) *ethyl acetate*, by polymerization in the presence of aluminium ethoxide,



In addition to the above three compounds, a number of other important aliphatic compounds of simple constitution have been obtained from acetylene, *via* acetaldehyde (*q.v.*) More complex substances, such as *artificial rubber*, have also been obtained by this means.

(b) Conversion of acetylene into *benzene* at a dull red heat [Sec. 92] may some day prove to be of great commercial importance, though so far it cannot be said to possess any practical significance.

(c) Conversion of acetylene into heterocyclic compounds, *thiophene* and *pyrrole*.

(d) Combination of acetylene with chlorine in the presence of a catalyst yields acetylene tetrachloride, $\text{C}_2\text{H}_2\text{Cl}_4$, which is used extensively as a solvent under the name of *westron*. The latter is also employed in the preparation of other solvents, *e.g.*, *westrosol* (trichloroacetylene), $\text{CCl}_2\equiv\text{CHCl}$, and *acetylene dichloride*, $\text{CHCl}=\text{CHCl}$.

(4) Acetylene has recently been used by the Zeppelin factory at Friedrichshafen, Germany, for the manufacture of hydrogen. The process consists in decomposing acetylene contained in steel cylinders by electric sparks. The very fine carbon obtained as the by-product is used for making printer's ink.

Constitution. The constitution of acetylene follows from its formation from ethylene dibromide and acetaldehyde (Sec. 91), the two carbon atoms being linked together by a triple bond. The representation of the molecule by atomic models is shown in Fig. 59.

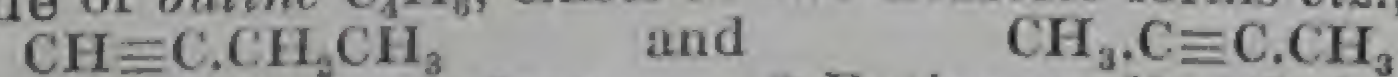


Fig. 59.

94. Homologues of Acetylene. The homologues of acetylene are divided into two distinct classes, *viz.*, mono-alkyl acetylenes and di-alkyl acetylenes. As already mentioned, the former class gives mono-metallic substitution compounds, while the latter are incapable of yielding such derivatives.

Allylene, *propine* or *methyl-acetylene*, $\text{CH}_3.\text{OC}\equiv\text{CH}$, is a gas boiling at 24° . When treated with concentrated sulphuric acid it yields mesitylene (Sec. 92).

Crotonylene or *butine* C_4H_6 , exists in two isomeric forms *viz.*,



1-Butine or ethylacetylene

2-Butine or dimethylacetylene

The first of these boils at 18° and the second at 28° .

94A. Diacetylenes. The diacetylenes contain two triple bonds, and have the general formula $\text{C}_n\text{H}_{2n-6}$, which is identical with that of the benzene hydrocarbons. In chemical behaviour, the hydrocarbons of this series resemble acetylenes, and combine with four monovalent atoms or groups. They polymerize with great ease.

Diacetylene, *butadiene*, $\text{CH} : \text{C} : \text{C} : \text{CH}$, is a gas of a peculiar odour. It can be readily converted into a liquid which boils at 10° . It yields a violet-red copper compound and a yellow silver compound, the latter exploding on being rubbed, even when moist.

Dipropargyl¹, 1 : 5-*Hexadiene*, $\text{CH} : \text{C} : \text{CH}_2\text{CH}_2\text{C} : \text{CH}$, possesses a special interest, as it is isomeric with benzene, C_6H_6 .

QUESTIONS

1. Write a note on the nomenclature of unsaturated hydrocarbons.
2. What do you understand by *unsaturation* in organic compounds? What reactions are characteristic of this state? (*Punjab, Inter., 1920*)
3. Give the general methods of formation of the olefine hydrocarbons and their chief reactions.
4. Describe the laboratory methods for the preparation of ethylene. Name three of its characteristic properties. (*Punjab, Inter., 1931*)
5. How can ethylene be prepared on a commercial scale? Give its important uses.
6. 12 c.c. of a gaseous hydrocarbon were mixed with 90 c.c. of oxygen, and the mixture exploded. After explosion, the volume was 72 c.c. On adding KOH, 36 c.c. of gas disappeared, leaving oxygen only. What is the molecular formula of the gas? All the above measurements were made at 15°C and 755 mm. pressure, the gases being saturated with moisture. [Aq. tension at $15^\circ\text{C} = 12.7$ mm.] (*Punjab, Inter., 1919*)
7. A liquid hydrocarbon was found to contain 85.7 per cent. of carbon. Its vapour density was 35. It decolorized dilute alkaline potassium permanganate solution and bromine water. When treated with ozone and dilute hydrochloric acid, it gave both acetaldehyde and acetone. What hydrocarbon was it?
8. Give the general methods of the preparation of acetylene hydrocarbons and their chief chemical properties. Into how many classes are the acetylene hydrocarbons divided, and in what important respects do the members of one class differ from those of the other?
9. How will you show that acetylene is formed (i) by the direct combination of its constituent elements, (ii) by the incomplete combustion of coal-gas, (iii) by the incomplete combustion of ether?
10. Write a comprehensive account of the various uses to which acetylene is put at the present day, and also those to which it is likely to be put in the near future.
11. A hydrocarbon was found to contain C, 88.9 per cent; H, 11.1 per cent. On being treated with excess of bromine it gave a compound containing 79.3 per cent of bromine. With ammoniacal silver solution it gave a white precipitate. What is the hydrocarbon?
12. A hydrocarbon containing 88.9 per cent of carbon was found to give no precipitate with ammoniacal solutions of silver nitrate and cuprous chloride. When its solution in concentrated sulphuric acid was diluted with water and distilled, methyl ethyl ketone passed over. The vapour density of the hydrocarbon was 27. What hydrocarbon was it?

ANSWERS

6. C_3H_6 .
7. Trimethyl-ethylene, $(\text{CH}_3)_2\text{C} = \text{CH} \cdot \text{CH}_3$.
11. Ethyl-acetylene, $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$.
12. Dimethyl-acetylene, $\text{CH}_3\text{C} \equiv \text{C} \cdot \text{CH}_3$.

¹ The monovalent group, $\text{CH} : \text{C} : \text{CH}_2$ derived from propine, $\text{CH} : \text{C} : \text{CH}_3$, is termed *propinyl* or *propargyl*.

(Love 12011 No. 11. 2nd Year)

CHAPTER XII

HALOGEN DERIVATIVES OF HYDROCARBONS

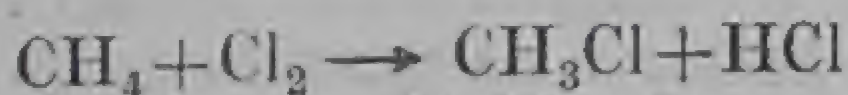
The halogen derivatives of the aliphatic hydrocarbons provide the most valuable starting material for the syntheses of aliphatic compounds, and, for this reason, are dealt with before any other class of derivatives.

HALOGEN DERIVATIVES OF PARAFFINS

95. Monohalogen Derivatives. These are derived from the paraffin hydrocarbons by the replacement of only one hydrogen atom by a halogen atom. They may also be regarded as *esters* of the halogen acids, and, for this reason, they are more commonly called alkyl halides.

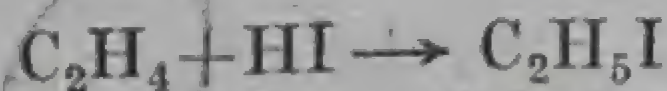
96. Formation of Alkyl Halides. Alkyl halides are obtained by the following general methods:—

(1) From *paraffins*, by the action of halogens in the presence of sunlight; *e.g.*,

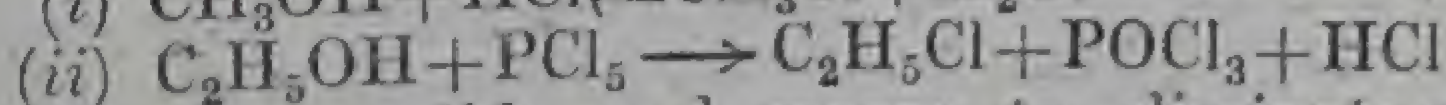
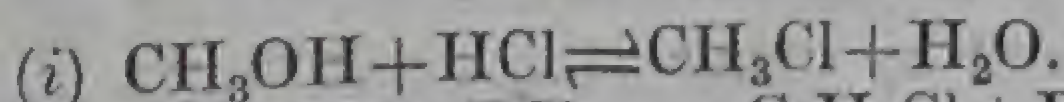


The reaction, however, is *not* suitable for preparing alkyl halides, since it proceeds further to give difficultly separable mixtures of isomerides and higher halogen derivatives.

(2) From *olefines*, by the direct combination with halogen hydroacids; *e.g.*,



(3) From *alcohols*, by the action of halogen acids or phosphorus halides:



Reaction (i) is reversible and means to eliminate water must be adopted. In Grove's process, for preparing alkyl chlorides, alcohol, to which some anhydrous zinc chloride has been added, is saturated with gaseous hydrogen chloride. Another method consists in distilling a mixture of alcohol, sodium halide and concentrated sulphuric acid (see Expt. 32, Sec. 98).

In Sabatier and Mailhes' method, the esterification is effected catalytically by passing a mixture of alcohol vapour and hydrogen chloride over alumina heated at 400° to 450° (compare Sec. 78). In

this method, a mixture of the isomeric alkyl chlorides is obtained together with the corresponding olefine hydrocarbon. Propyl alcohol yields mainly isopropyl chloride, a small amount of propyl chloride being also formed.

When preparing alkyl bromides by reaction (ii) it is not necessary to employ previously prepared phosphorus halides; the halogen is gradually added to a mixture of alcohol and phosphorus, and the whole is then warmed to complete the reaction.

(4) From *alkyl sulphates*, by the action of the metallic halides in aqueous solution:

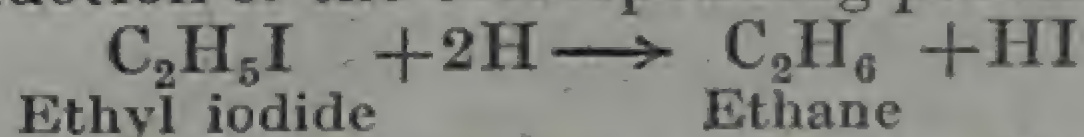


97. Properties of Alkyl Halides. *Physical.* Only a few of the alkyl halides, *viz.*, CH_3Cl , $\text{C}_2\text{H}_5\text{Cl}$ and CH_3Br , are gases under ordinary conditions, but the majority are colourless pleasant-smelling liquids. Those having a high molecular weight are solids, *e.g.*, cetyl iodide, $\text{C}_{16}\text{H}_{33}\text{I}$. Among halides derived from a particular alcohol, the chloride has the lowest boiling point; the bromide boils about 22° , and the iodide 50° , higher than the chloride. Specifically, also, the iodides are heaviest and the chlorides lightest. Like other esters, alkyl halides are practically insoluble in water, but they readily dissolve in alcohol, ether, carbon disulphide, and other organic solvents.

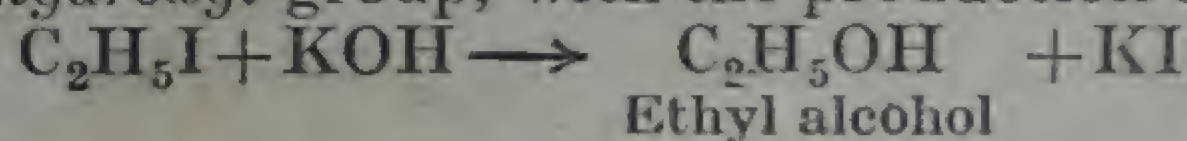
Chemical. (a) **Non-polar Character.** Alkyl halides differ characteristically from the metallic halides. As is well known, the latter compounds react instantaneously with aqueous silver nitrate, yielding a precipitate of silver halide. Alkyl halides, on the other hand, being non-electrolytes, either do not react with silver nitrate or the reaction proceeds very slowly.

(b) **Substitution Reactions.** It must not be concluded from (a) that the halogen in alkyl halides is particularly firmly bound. As a matter of fact, the aliphatic halogen compounds are amongst the most reactive of all organic compounds. The halogen atom is easily removed and replaced by other atoms or groups. This property renders them of great importance in synthetic organic chemistry, as is illustrated by the following reactions:—

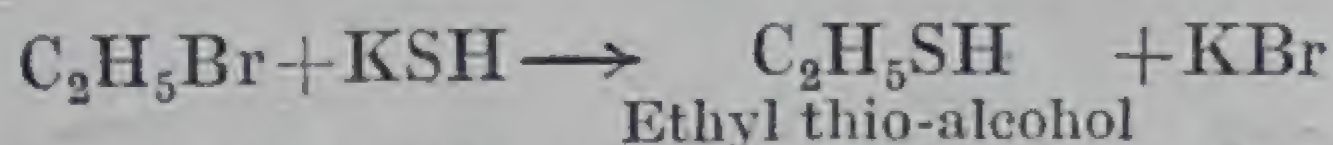
(1) When an alkyl halide is treated with zinc-copper couple and alcohol or tin and hydrochloric acid, the halogen atom is replaced by *hydrogen* with the production of the corresponding paraffin (*cf.* Sec. 72); *e.g.*,



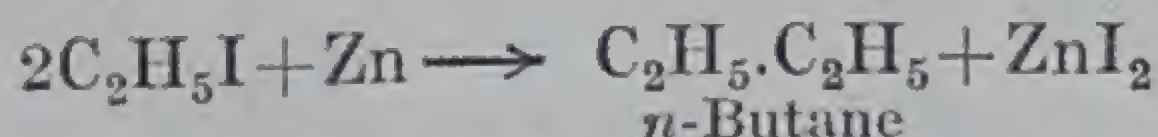
(2) When heated with aqueous potash, the halogen atom is replaced by the *hydroxyl* group, with the production of an alcohol; *e.g.*,



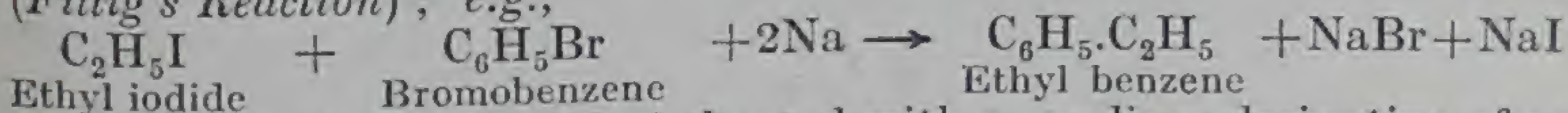
(3) When an alkyl halide is distilled with potassium hydrosulphide, the halogen is replaced by the *SH* group with the production of a thio-alcohol :—



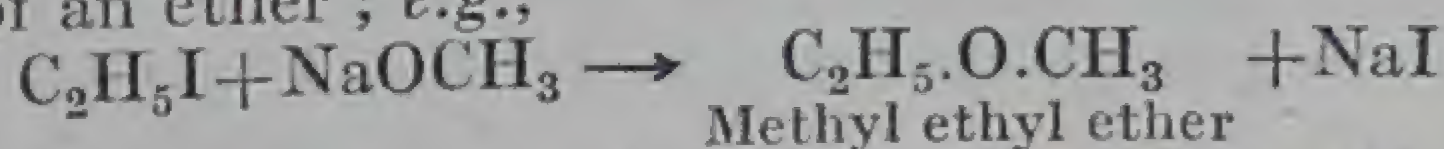
(4) When an alkyl halide is heated with sodium or zinc, the halogen atom of one molecule gets replaced by the *alkyl* group of the other, with the production of a higher paraffin (*Wurtz' Synthesis*); *e.g.*,



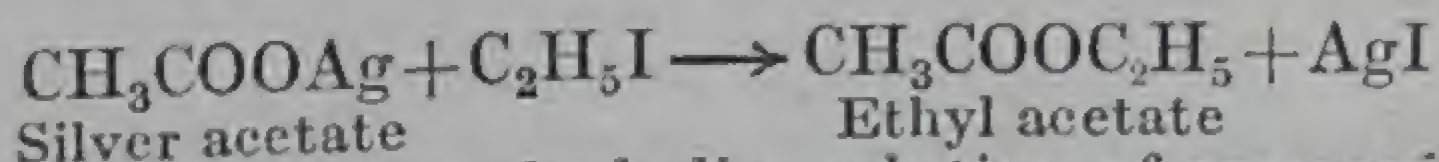
Similarly, when an alkyl halide is heated with a halogen derivative of a benzene hydrocarbon along with metallic sodium and dry ether, the halogen atom of the alkyl halide gets replaced by an *aryl* group, a higher homologue of benzene hydrocarbon being thus produced (*Fittig's Reaction*); *e.g.*,



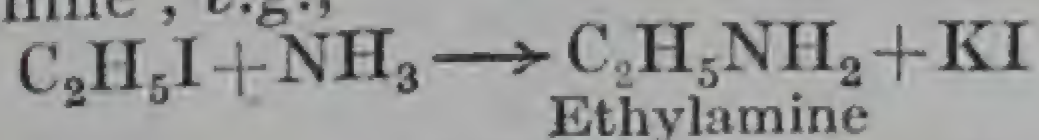
(5) When an alkyl halide is heated with a sodium derivative of an alcohol, the halogen atom is replaced by an *alkoxyl* group, with the production of an ether; *e.g.*,



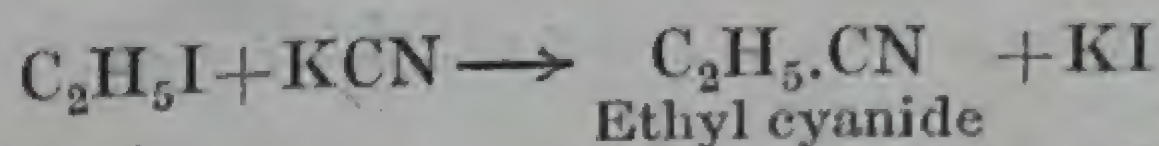
(6) Similarly, with silver salt of a carboxylic acid, the halogen atom gets replaced by an *acyloxyl* group, an ester being thus produced; *e.g.*,



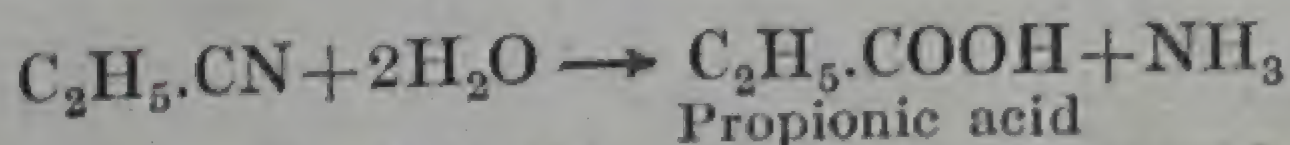
(7) When heated with an alcoholic solution of ammonia in a sealed tube, the halogen atom is replaced by an *amino* group with the production of an amine; *e.g.*,



(8) When heated with potassium cyanide, the halogen atom is replaced by the *cyano* group with the production of an alkyl cyanide; *e.g.*,

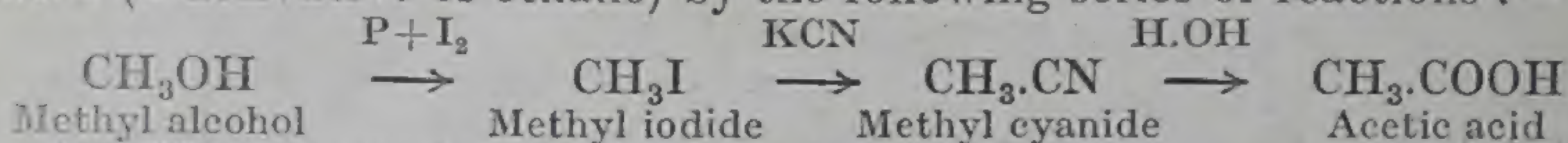


This reaction is of great importance, for the alkyl cyanides are easily converted into *carboxylic acids* by hydrolysis with mineral acids or alkalies :—

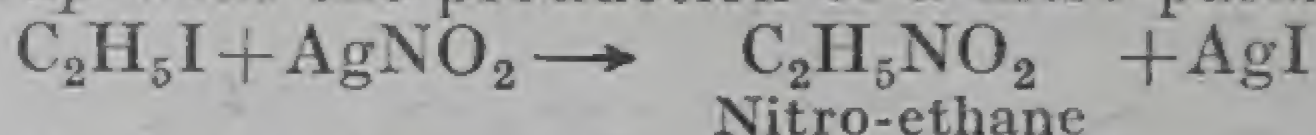


The conversion of an alkyl halide into alkyl cyanide involves the introduction of an additional atom of carbon into the molecule.

Hence, it affords a means of ascending a homologous series. Thus, methyl alcohol (a derivative of methane) may be converted into acetic acid (a derivative of ethane) by the following series of reactions :—



(9) When heated with silver nitrite, the halogen atom is replaced by the *nitro group* with the production of a nitro-paraffin ; *e.g.*,



(c) **Other Reactions.** The many-sided reactivity of alkyl halides and their use in synthetic organic chemistry is further shown by the following reactions that they undergo :—

1. *Conversion into Olefine Hydrocarbons.* See Sec. 79.

2. *Grignard's Reaction.* When a dry ethereal solution of an alkyl halide is treated with dry magnesium, a *magnesium alkyl halide* is produced ; *e.g.*,

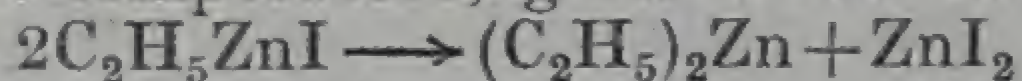


Magnesium alkyl halides themselves are extremely important synthesizing agents, and are employed for preparing a large number of organic compounds, under the name of Grignard's reagents (see next Chapter).

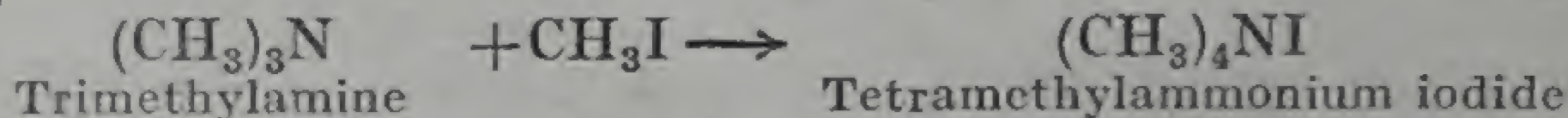
3. *Formation of Zinc Alkyls.* When an alkyl halide is heated with zinc filings in an atmosphere of carbon dioxide, a *zinc alkyl halide* is formed,



which, on raising the temperature, gives a *zinc alkyl*,

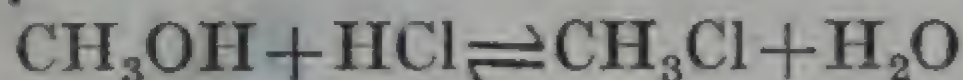


4. *Combination with Tertiary Amines.* Alkyl halides undergo direct addition with tertiary amines, forming quaternary ammonium salts ; *e.g.*,



98. Individual Members. A few of the alkyl halides in common use are given below. They all show the chemical properties given in the preceding article.

Methyl Chloride, or *Chloromethane*, CH_3Cl , is prepared by Grove's process : Methyl alcohol to which about half its weight of zinc chloride has been added, is saturated with hydrogen chloride. The mixture is then gently warmed over a water-bath, when methyl chloride passes over.



Methyl chloride is a colourless, sweet-smelling gas, which, on being cooled under pressure, condenses to a liquid boiling at -23° . Rapid evaporation of the liquid causes an intense heat absorption. The gas burns with a green-edged flame.

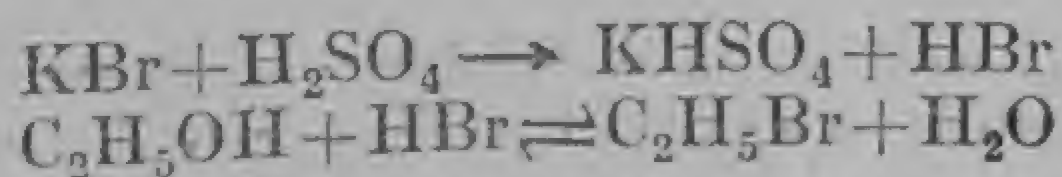
Uses. Methyl chloride is placed on the market in the liquid form. It is largely employed :—

- (1) As a methylating agent¹ in the manufacture of dyes, and
- (2) For the production of low temperatures.

Methyl Bromide. CH_3Br , resembles ethyl bromide in its method of preparation and properties. It boils at 4.5° .

Ethyl chloride. $\text{C}_2\text{H}_5\text{Cl}$, is also prepared by Grove's process. It is a liquid boiling at 12° . The rapid evaporation of the liquid causes an intense heat absorption as in the case of methyl chloride. For this reason, it is employed as a local anæsthetic.

Ethyl bromide. $\text{C}_2\text{H}_5\text{Br}$, is readily obtained by distilling a mixture of potassium bromide, ethyl alcohol and concentrated sulphuric acid.



Expt. 32. Place 30 c.c. of concentrated sulphuric acid in a distillation flask, add gradually 30 c.c. of alcohol with constant shaking and cooling. Then add 30 gm. of coarsely powdered potassium bromide. Connect the flask to a Liebig condenser, and the latter to an adapter dipping under ice-cold water in a flask (Fig. 60). Heat the flask on a sand bath. Ethyl bromide passes over and collects as a heavy oily layer at the bottom of the water in the receiver.

Separate the oil by means of a tap-funnel, wash it first with its own volume of water, then with dilute sodium carbonate solution, and finally with water. Allow the oil to stand over granular calcium chloride, until it becomes clear. Then decant it into a distillation flask, and redistil. Collect the fraction passing over at 37° — 40° , and seal it in a glass tube.

Ethyl bromide is a colourless, pleasant-smelling liquid (b.p. 38°).

Methyl Iodide. CH_3I , is prepared by gradually adding iodine to a mixture of methyl alcohol and red phosphorus, and distilling the

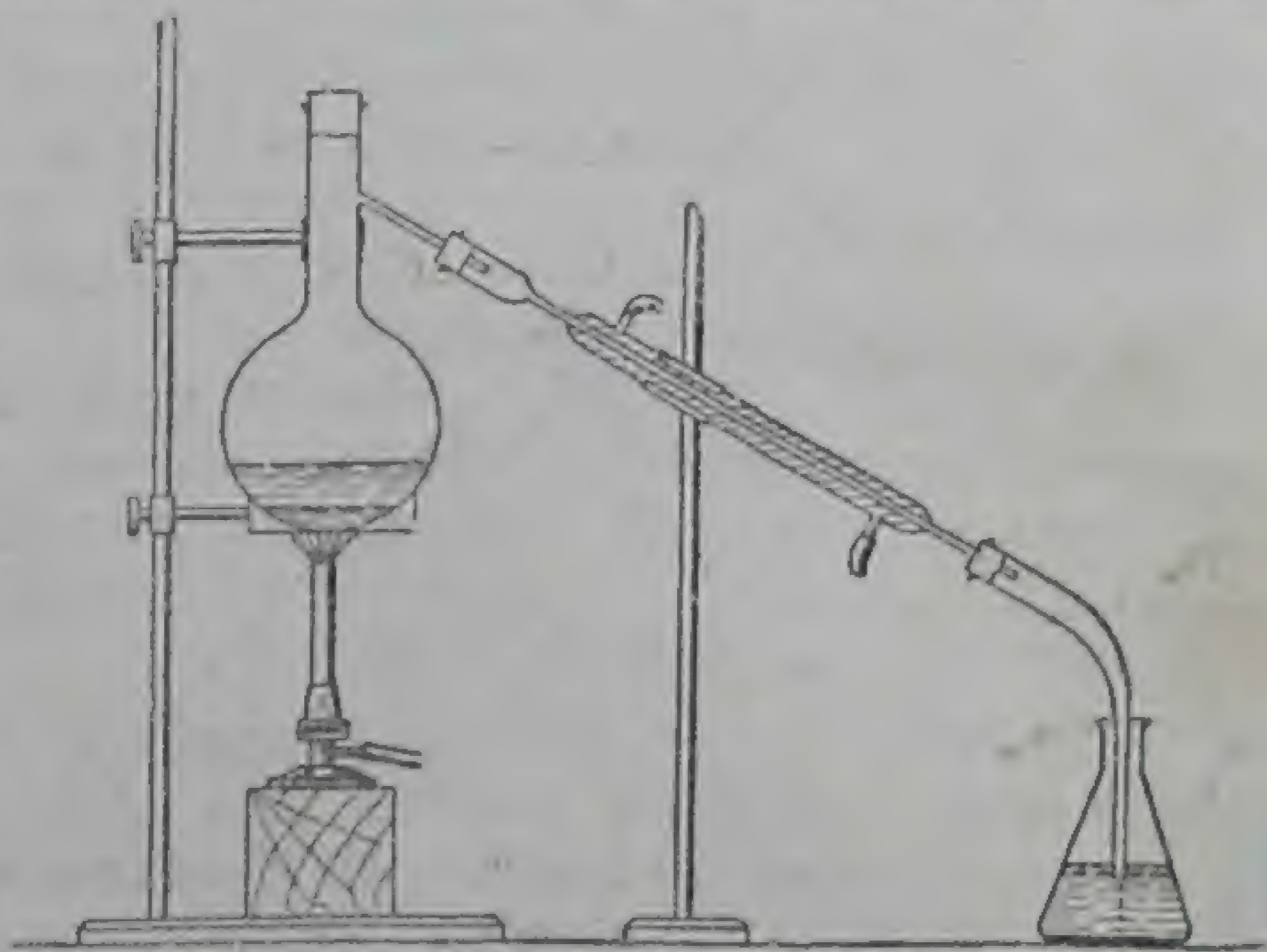
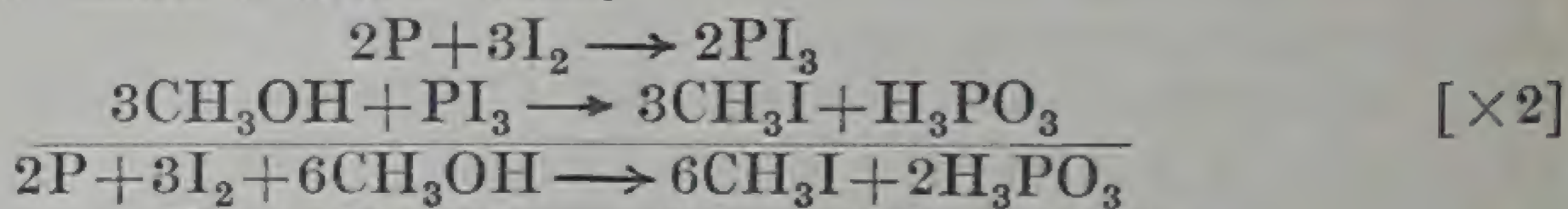


Fig. 60. Preparation of Ethyl Bromide.

¹ For introducing methyl group in a molecule.

reaction product from a water bath.



Expt. 33. *Preparation of Methyl Iodide* :—

Methyl alcohol, 22 c.c.

Red phosphorus, 5 gm.

Iodine, 50 gm.

Fit up the apparatus shown in Fig. 61. Put methyl alcohol and red phosphorus into the round-bottom flask (R), place the iodine on a plug of glass-wool covering the lower part of the funnel-tube (F), turn on a rapid stream of cold water into the condenser, and heat the water-bath. The vapour of boiling methyl alcohol rises through the side-tube (ST) up into the condenser; the condensate continuously drops on to the iodine in F, and thus gradually introduces it into the flask in the form of solution. When the reaction is complete, distil the product from a water bath.

Purify the methyl iodide as described under ethyl bromide.

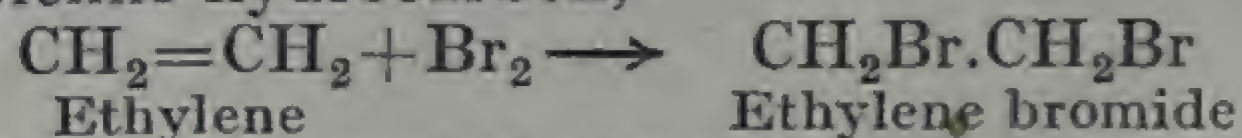
Methyl iodide is a colourless, highly refracting liquid having a sweetish odour (b. p. 42°). On exposure to light, it gradually darkens owing to the separation of iodine—a phenomenon common to nearly all organic compounds containing iodine.

Methyl iodide is used in the laboratory as a methylating agent, in preference to methyl chloride. The ease with which it can be handled and its greater reactivity more than make up for its greater cost.

Fig. 61. Preparation of Methyl iodide.

Ethyl Iodide, $\text{C}_2\text{H}_5\text{I}$, closely resembles methyl iodide and is prepared by using ethyl alcohol instead of methyl alcohol in the above experiment. It boils at 72° , and forms ethyl mercuri-iodide, Et. HgI , m.p. 182° . It is used in synthetic organic chemistry in the same way as methyl iodide.

99. Dihalogen Derivatives. The dihalogen derivatives of the paraffins may be divided into *two groups*, according as the two halogen atoms are in union with the same or with different carbon atoms. The latter class is obtained by the direct combination of a halogen with an olefine hydrocarbon,



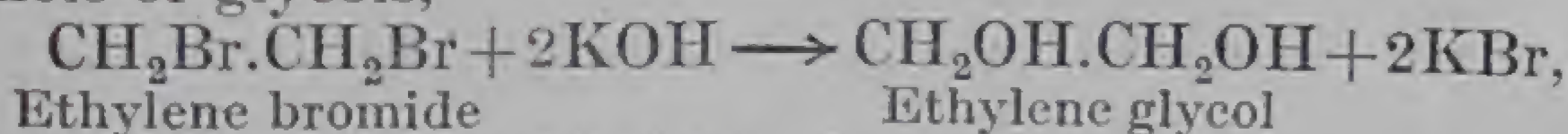
while the former may be prepared either from an acetylene hydrocarbon by making it combine with two molecular proportions of a halogen hydride,



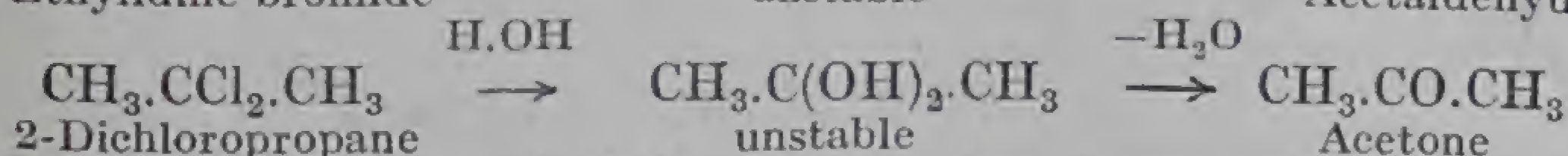
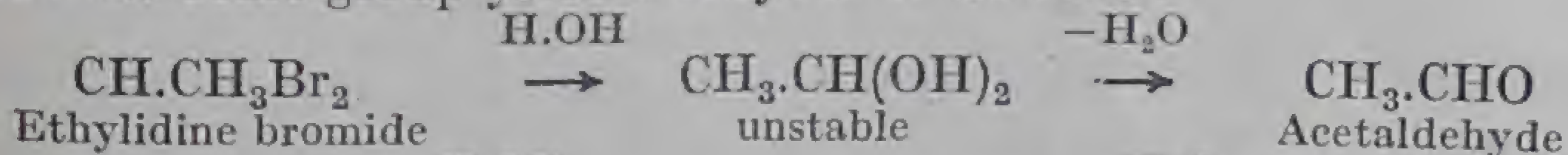
or from an aldehyde or a ketone by the action of phosphorus pentahalide.



On being heated with aqueous alkalies, the derivatives containing the halogen atoms linked to two different carbon atoms, yield dihydric alcohols or glycols,



while the other group yield aldehydes or ketones :



Dichloroethane, $\text{C}_2\text{H}_4\text{Cl}_2$ exists in two forms : (1) 1 : 2-*dichloroethane* or ethylene chloride, $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$, and (2) 1 : 1-*dichloroethane* or ethylidene chloride, $\text{CH}_3.\text{CHCl}_2$.

Their respective methods of preparation have already been given. The *constitution* of each compound follows from the product obtained by its hydrolysis.

Ethylene Bromide, $\text{CH}_2\text{Br}.\text{CH}_2\text{Br}$, is obtained by passing ethylene into bromine. It is a colourless, pleasant-smelling liquid, boiling at 131° . It is much used as a solvent and for synthetic purposes.

100. Trihalogen Derivatives. Of the trihalogen derivatives of paraffin hydrocarbons the most important are : (1) Chloroform, CHCl_3 , (2) Bromoform, CHBr_3 , and (3) Iodoform, CHI_3 .

Chloroform or *Trichloromethane*, CHCl_3 . This compound is prepared both on a commercial scale and in the laboratory by distilling alcohol or acetone with bleaching powder.

Expt. 34. 100 grams of bleaching powder are rubbed into a paste with about 400 c.c. of water and placed in a two-litre flask, fitted with a condenser, an adapter, and a receiver (Fig. 62). 25 c.c. of alcohol or acetone are added, and the mixture gradually heated on a sand bath. If there are any signs of frothing, the flame should be temporarily removed, until the reaction moderates. The heating is continued, until no more chloroform distils over. The product is separated from the aqueous layer, shaken with dilute alkali, dried over calcium chloride, and redistilled.

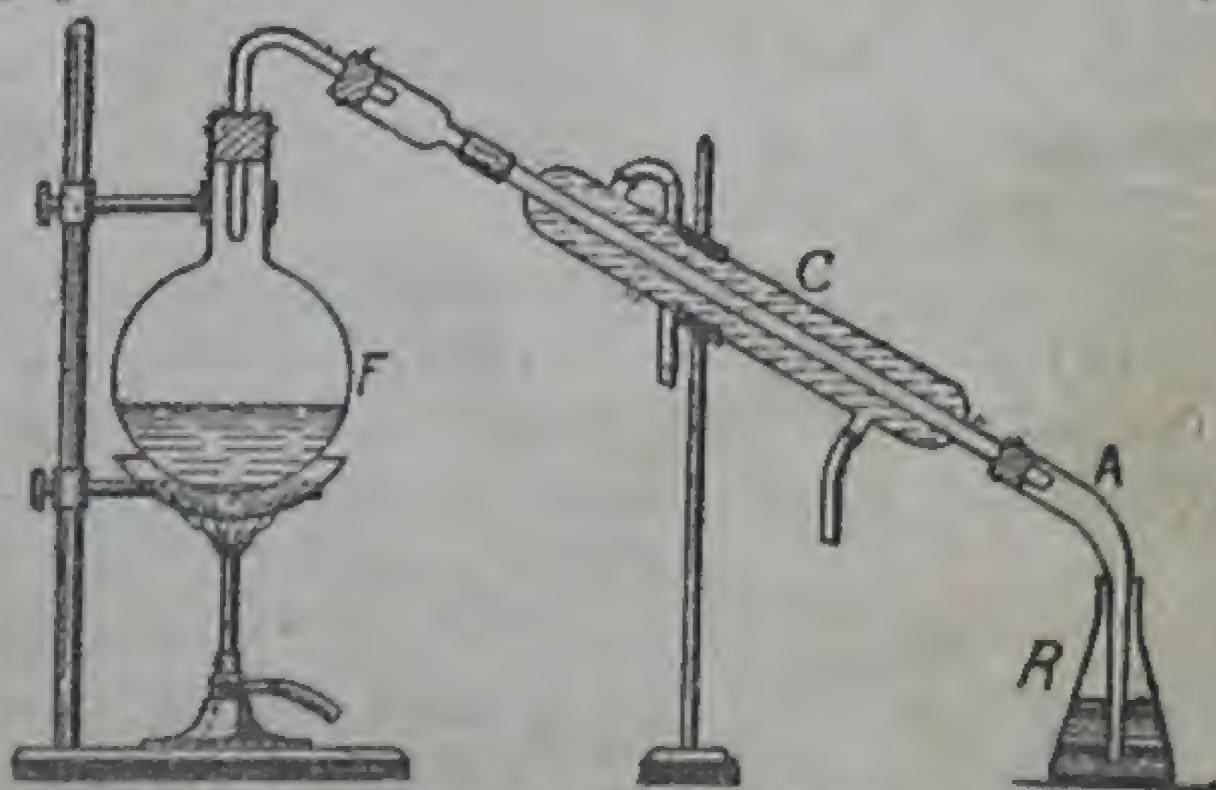
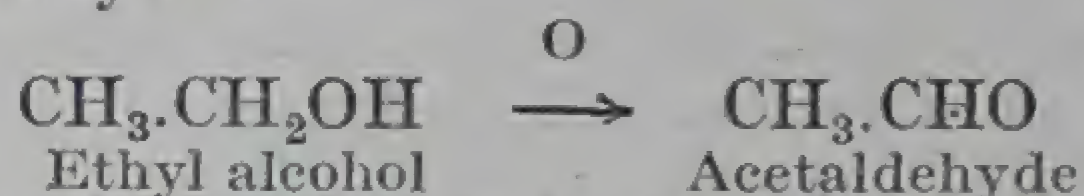


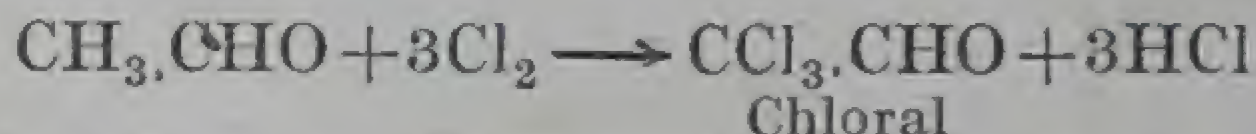
Fig. 62. Preparation of Chloroform.

The mechanism of the reaction in the case of alcohol is assumed to be as follows :

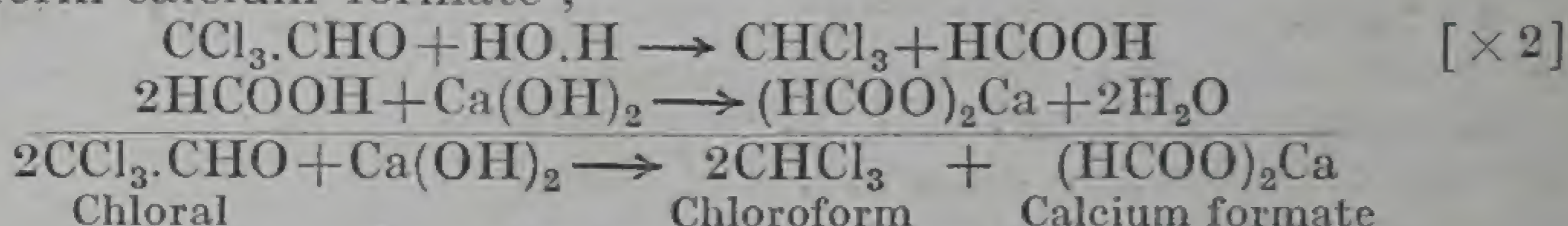
Step I. Ethyl alcohol is oxidized by chlorine of the bleaching powder to acetaldehyde :



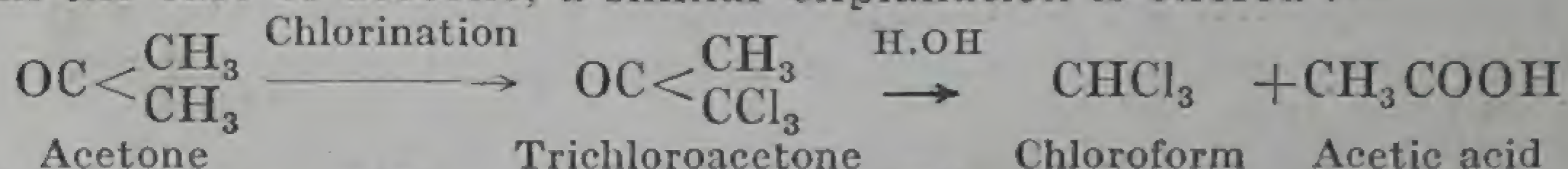
Step II. The acetaldehyde gets chlorinated to trichloro-acetaldehyde (chloral) :



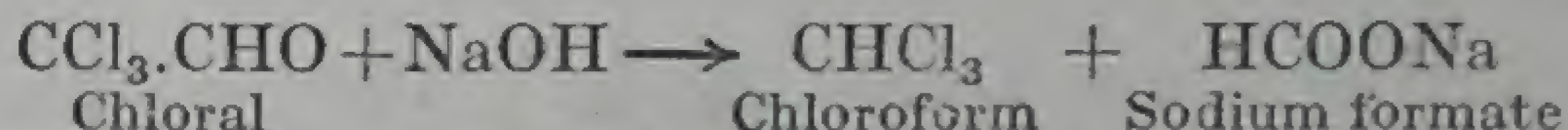
Step III. The chloral is hydrolysed by the lime present in bleaching powder to chloroform and formic acid, the latter combining with lime to form calcium formate :



In the case of acetone, a similar explanation is offered :—



Preparation of Pure Chloroform. Chloroform prepared as above is generally impure. A convenient though expensive method of preparing pure chloroform consists in heating chloral or chloral hydrate with a solution of caustic soda.



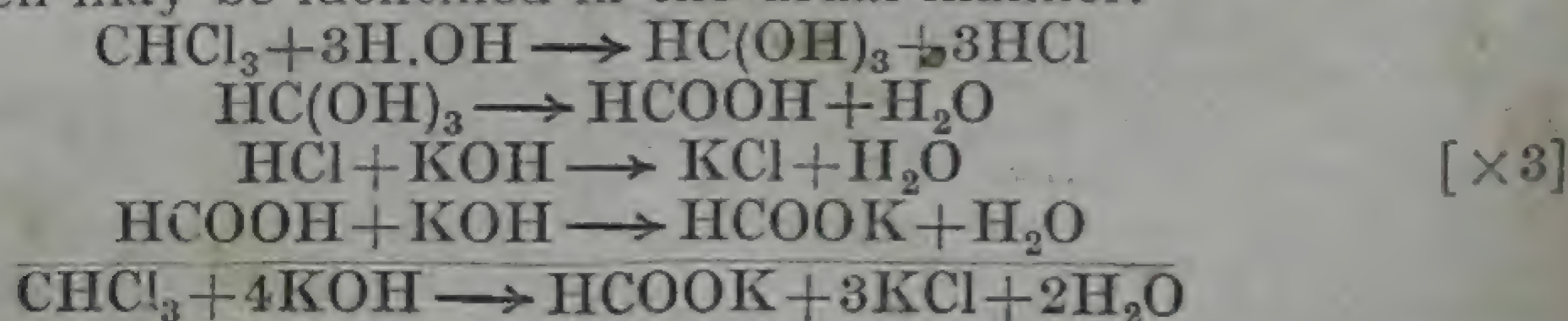
Physical Properties. Chloroform is a colourless liquid having a sweet sickly odour and a sp. gr. of 1.5 at 15°. It boils at 61°, and burns with a green-edged flame. It is soluble in about 200 volumes of cold water, to which it imparts a sweet taste.

Reactions. The more important reactions of chloroform are :—

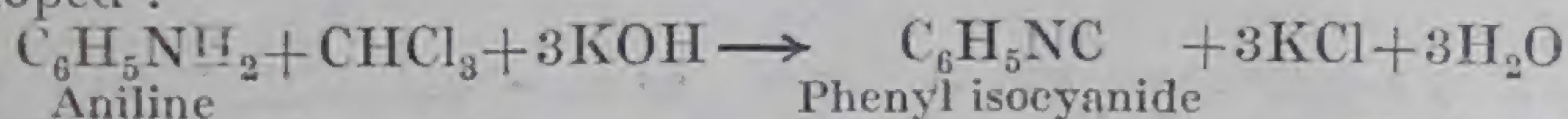
(1) *Oxidation.* Under the influence of air and light, chloroform is decomposed into hydrochloric acid and the highly poisonous substance carbonyl chloride :—



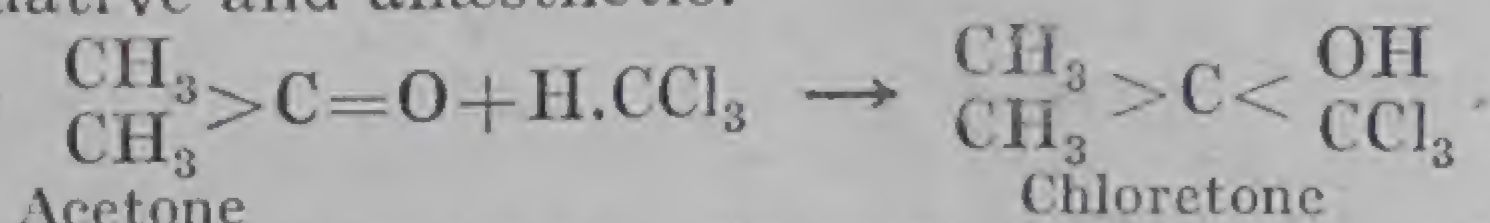
(2) *Hydrolysis.* When heated with alcoholic potash under a reflux condenser, it is hydrolysed into potassium formate and potassium chloride, which may be identified in the usual manner.



(3) *Carbylamine Reaction*. When a drop of chloroform is warmed with a drop of aniline and a few drops of alcoholic potash, a disgusting odour of phenyl isocyanide or carbylamine, C_6H_5NC , is developed :—



(4) *Condensation with Acetone*. In the presence of alkali, chloroform undergoes condensation with acetone, yielding *trichloro-tertiary-butyl alcohol*, known as *chloretone*, which is sometimes used in medicine as a sedative and anæsthetic.



(5) *Substitution Reactions*. Chloroform reacts with chlorine to form carbon tetrachloride, CCl_4 , with concentrated nitric acid to form chloropierin, CCl_3NO_2 , and with nascent hydrogen ($Zn + HCl$) to give methylene chloride, CH_2Cl_2 .

Tests. Reactions (2) and (3) are both employed as tests for chloroform. The latter is extraordinarily sensitive and will detect 1 part of chloroform in 5,000 parts of alcohol. It is, however, not conclusive, as it is also given by bromoform, iodoform, chloral, trichloroacetic acid and other substances, that yield chloroform in the presence of alkali.

In the case of reaction (2) a few drops of the product of hydrolysis is tested for the chloride radical with silver nitrate; the remainder is then neutralized exactly, and heated with mercuric chloride solution. The formation of a precipitate of mercurous chloride and metallic mercury shows the presence of a formate.

Test for impurities. Chloroform for anæsthetic purpose must be of the highest degree of purity. When shaken with water, the aqueous layer should not turn blue litmus red, nor should it give any cloudiness with silver nitrate. Further, it should not turn yellow when agitated for one hour with concentrated sulphuric acid; if the colour change occurs, it shows the presence of aldehyde, methyl alcohol, etc.

Storing of Chloroform. To avoid oxidation, (See Reaction 1) the following precautions must be observed in storing chloroform for use as an anæsthetic :—

- (a) It is mixed with about 1 per cent of ethyl alcohol, which serves as a retarder.
- (b) The bottles must be filled almost to the stopper. This serves to exclude air.
- (c) It is kept in the dark, or in bottles of amber colour.

Uses. Chloroform is used—

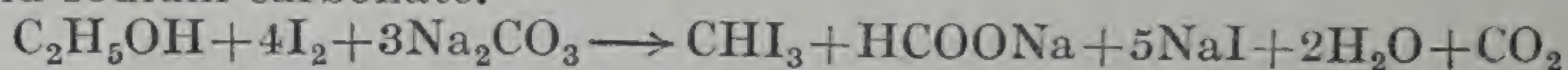
1. as an anæsthetic,
2. as a preservative for animal or vegetable infusions or decoctions,
3. as a flavouring agent to disguise the taste of nauseous medicines,

4. as a solvent for organic substances both in the laboratory and industry.

Bromoform, CHBr_3 . Bromoform is prepared in a similar manner to chloroform by the action of bromine on alcohol or acetone. It is a colourless sweet liquid, soluble in alcohol, but very slightly so in water. It boils at 151° . It is used in medicine for whooping cough.

Iodoform, CHI_3 .

Preparation. (1) Iodoform is prepared both in the laboratory and on the commercial scale by warming a mixture of iodine, alcohol and sodium carbonate.¹



Expt. 35. Preparation of Iodoform—

Ethyl alcohol or acetone, 5 gm.

Sodium carbonate crystals, 20 gm.

Iodine, 10 gm.

Water 50 c.c.

Dissolve the sodium carbonate and alcohol (or acetone) in water, and gradually add the iodine to the solution. During the addition, the temperature is gradually raised to 80° , but not higher, since iodoform is readily hydrolysed. When the deep, brown colour of iodine has disappeared, the liquid is allowed to cool and the crystals of iodoform filtered. They are then washed with a little distilled water, and finally purified by recrystallization from alcohol.

(2) A modern method of preparing iodoform consists in electrolysis of an aqueous-alcoholic solution of potassium iodide and carbonate.

Properties. Iodoform crystallizes in lustrous, yellow, six-sided plates, having a strong characteristic smell, at 119°C . It sublimes readily, and is volatile at ordinary temperature. It is insoluble in water, but soluble in alcohol and ether.

In its chemical behaviour, iodoform is similar to chloroform. It gives the carbylamine reaction, and is hydrolysed by caustic potash, yielding potassium iodide and potassium formate. On reduction with hydriodic acid and phosphorus, it gives methylene iodide, CH_2I_2 .

Use. Iodoform is much used in surgery as an antiseptic.

101. Tetrahalogen Derivatives.

Carbon tetrachloride, tetrachloromethane, CCl_4 , is obtained on a commercial scale by the chlorination of carbon disulphide in the presence of anhydrous aluminium chloride, iron or iodine (which act as chlorine carriers) :



¹ The mechanism of the reaction is assumed to be similar to that given in the case of chloroform. The intermediate compound *iodal*, $\text{CI}_3\cdot\text{CHO}$, and analogous to chloral, has not been isolated.

Sulphur monochloride (b.p. 138°), which is here obtained as a by-product, is separated by fractional distillation. The carbon tetrachloride fraction is further purified by shaking with caustic soda and redistillation. Carbon tetrachloride is a colourless liquid boiling at 76° .

It is used on a large scale as a solvent, and in medicine as an anthelmintic. The use of carbon tetrachloride in putting out oil fires is illustrated in the following experiment :—

Expt. 36. Place some kerosene oil in a small dish, and set fire to it. Now pour a little carbon tetrachloride over the burning oil: the flame is at once extinguished.

Acetylene tetrachloride, tetrachloro-ethane, Westron, $C_2H_2Cl_4$.

This substance is prepared on a large scale by the direct combination of acetylene and chlorine. Since the combination between commercial¹ acetylene and chlorine occurs with explosive violence (Expt. 31), it is carried out in the presence of a catalyst, when it proceeds quite smoothly. In one of the processes a mixture of acetylene and chlorine in theoretical proportions is passed through a catalyst consisting of a mixture of iron turnings and an inert material, such as kieselguhr or broken quartz. The catalyst is placed in a steel tube cooled by a water jacket (Fig. 63). Acetylene tetrachloride is kept trickling constantly down the tube.

Acetylene tetrachloride is a heavy non-inflammable liquid. It is an excellent solvent for fats, oil resins and tarry substances.

Uses. (1) The main use of acetylene tetrachloride is in the manufacture of trichloro-ethylene or *westrosol* (Sec. 106) and other chlorine compounds.

(2) It is used as a solvent for cellulose-acetate varnishes, fats and rubber.

(3) It is also used as a paint remover and a degreaser for metals, textiles and other materials.

(4) Another use of this substance is as an insecticide, *e.g.*, for white fly on tomato plants and fur-weevil in barley.

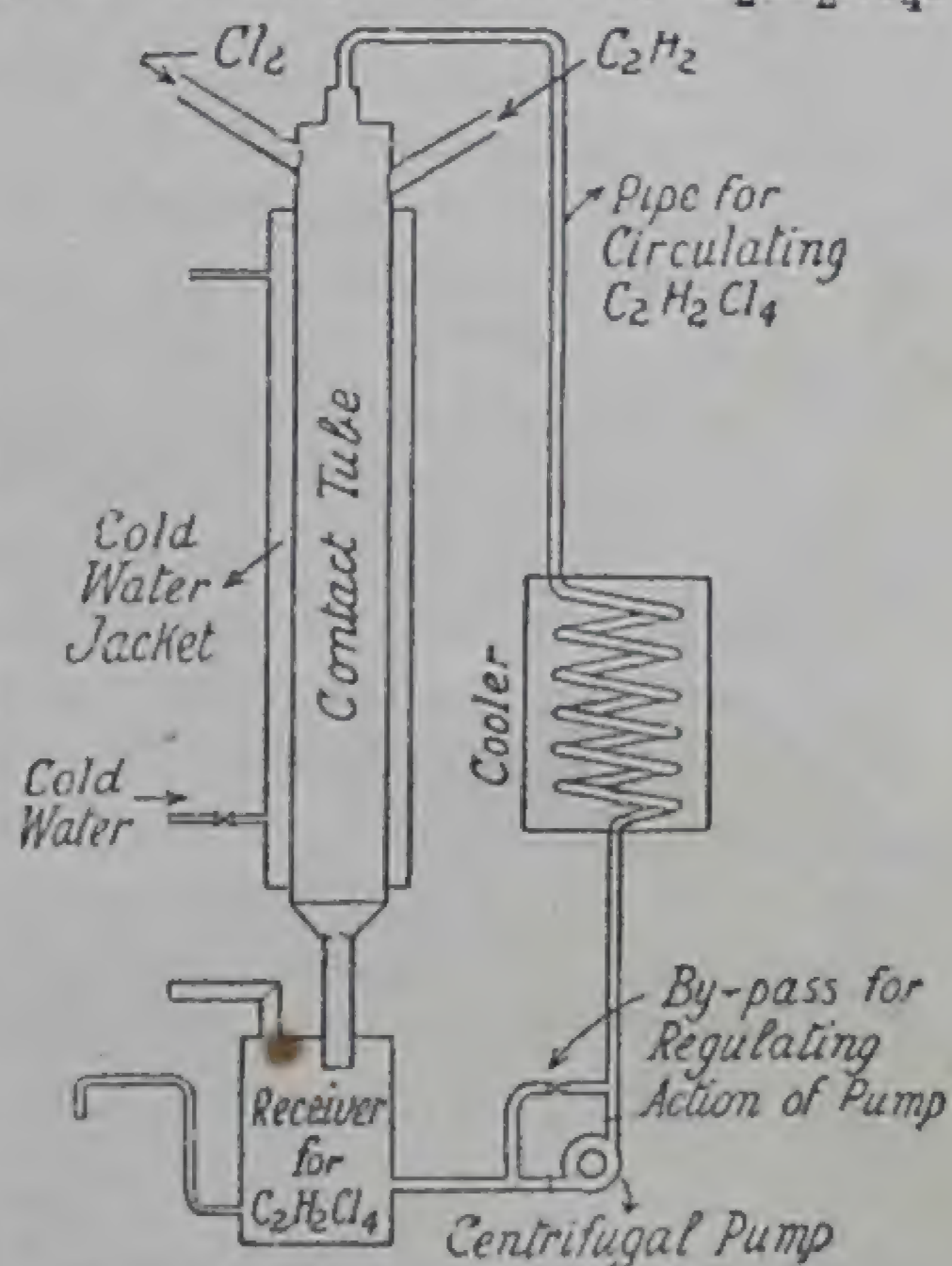


Fig. 63. Plant for the Manufacture of Westron.

¹ Pure acetylene and chlorine combine together smoothly.

HALOGEN DERIVATIVES OF UNSATURATED HYDROCARBONS

102. General. The unsaturated halogen compounds are derived from the unsaturated hydrocarbons by the replacement of hydrogen by one or more halogen atoms. They are divided into two distinct groups:

(i) The unsaturated halogen compounds *containing the halogen in the direct combination with a doubly (or triply) bound carbon atom*; e.g.,

$\text{CH}_2=\text{CHBr}$, Bromo-ethylene or *vinyl*¹ bromide;

$\text{CHBr}=\text{CH}.\text{CH}_3$, 1-Bromopropene;

$\text{CH}_2=\text{CBr}.\text{CH}_3$, 2-Bromopropene.

(ii) Those in which the *halogen is attached to a singly bound carbon atom*; e.g.,

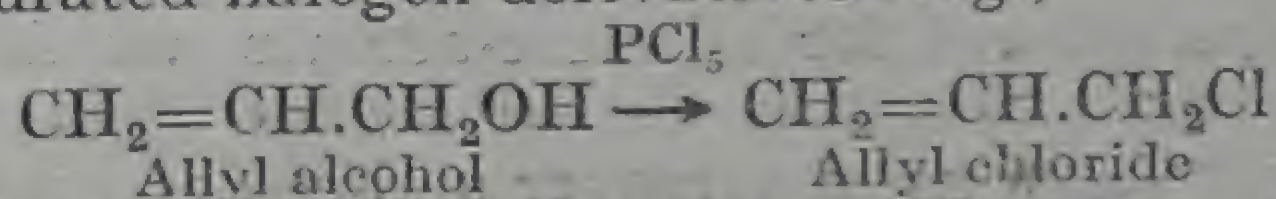
$\text{CH}_2=\text{CH}.\text{CH}_2\text{Br}$, 3-Bromopropene or *allyl*¹ bromide.

It should be carefully noted that while the halogen linked to a *singly* bound carbon atom, as in allyl bromide and the halogen derivatives of saturated hydrocarbons, is particularly adapted to double decompositions, being replaceable by OH, CN, NH_2 groups etc. (Sec. 97), the *halogen atom directly linked to a doubly bound carbon atom* as in vinyl bromide, *lacks this reactivity almost entirely*. Thus, alkalis do not convert these compounds into alcohols nor ethoxides into ethers.

Apart from the power to undergo double decomposition, the two classes of compounds show analogous behaviour. Thus, both classes react with alcoholic potash, yielding acetylene hydrocarbons. They also combine with dry magnesium in the presence of dry ether, forming Grignard's reagents (next Chapter). Further, they combine with halogen acids to give *addition* products. In the addition of a halogen acid, the halogen attaches itself to the carbon atom that carries the *least* number of hydrogen atoms (Markownikoff's rule, Sec. 85).

103. Formation. The halogen derivatives of unsaturated hydrocarbons, unlike those of the paraffins, cannot be obtained by the direct action of halogens on the hydrocarbons, owing to the formation of additive products. They may be obtained by three different methods:

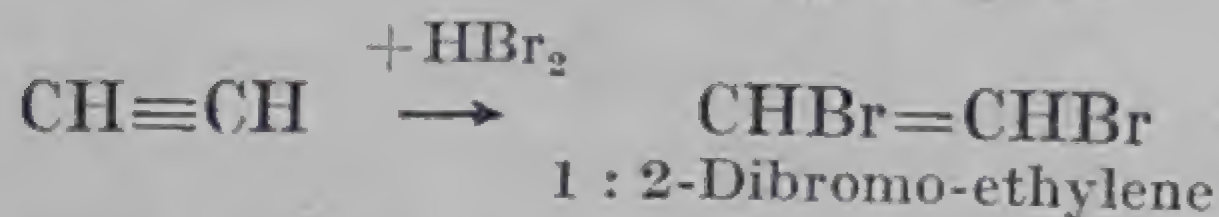
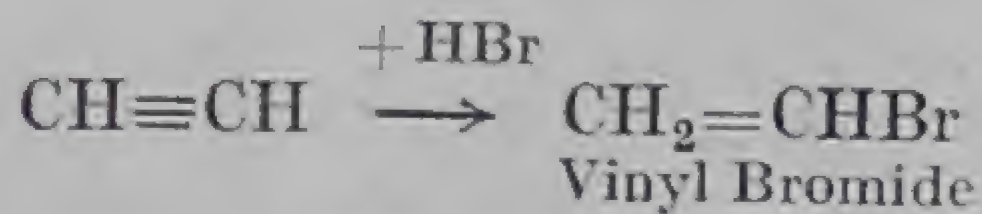
(1) *From an Unsaturated Alcohol.* When an unsaturated alcohol is treated with a halogen acid or a phosphorus halide, we get the corresponding unsaturated halogen derivatives: e.g.,



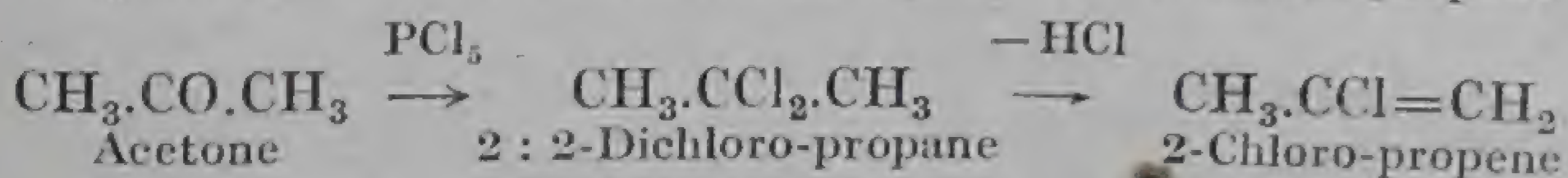
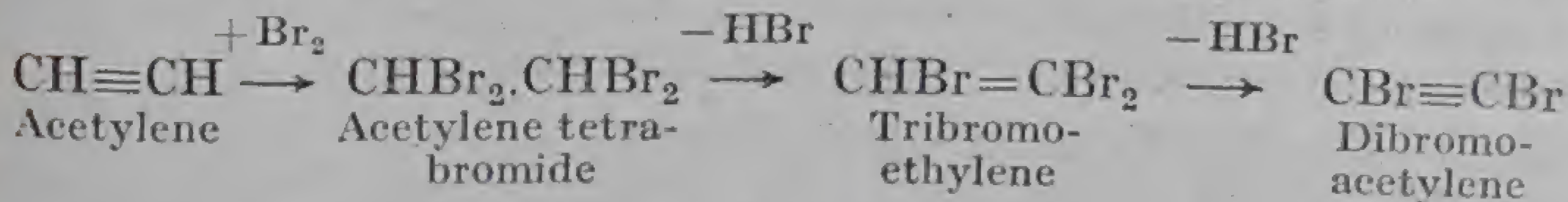
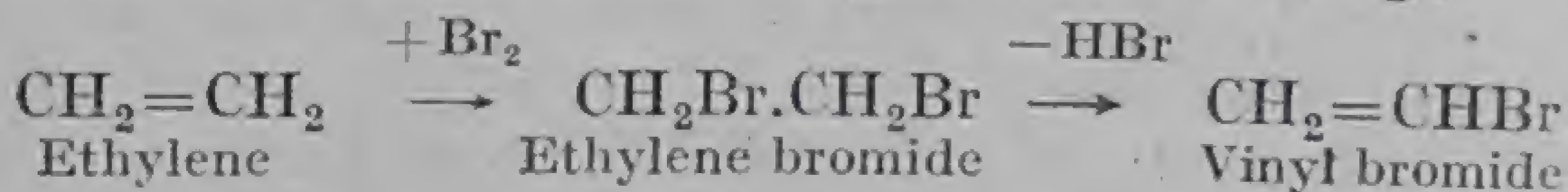
(2) *From an Acetylene Hydrocarbons.* When an acetylene hydrocarbon is treated with *one* molecular proportion of a halogen or a

¹ The monovalent ethene residue, $\text{CH}_2=\text{CH}'$, and propene residue $\text{CH}_2=\text{CH}.\text{CH}'_2$ are termed *vinyl* and *allyl* respectively.

halogen hydride, we get a halogen derivative of an ethylene hydrocarbon ; *e.g.*,



(3) *From a Saturated Polyhalogen Derivative.* When a polyhalogen derivative of a saturated hydrocarbon (obtained by the direct addition of a halogen to an unsaturated hydrocarbon or by the action of PCl_5 or PBr_5 on an aldehyde or ketone) is subjected to the moderated action of alcoholic potash, a partial removal of the halogen hydride occurs with the production of an unsaturated halogen derivative ; *e.g.*,



The constitution of an unsaturated halogen derivative follows from its method of production.

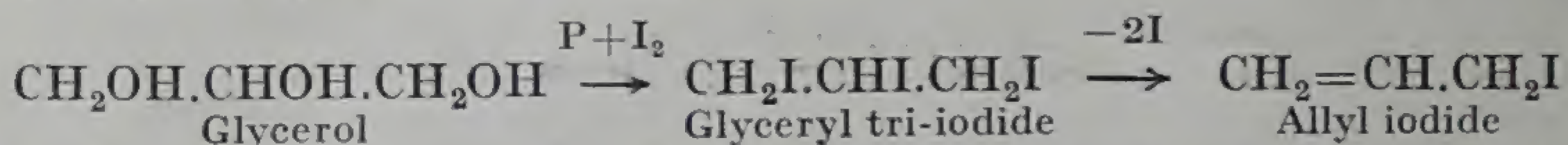
104. Vinyl Halides, $\text{CH}_2=\text{CHX}$.

Vinyl Chloride is gaseous at ordinary temperatures. It does not react with an aqueous solution of caustic alkalies nor with sodium ethoxide, etc. In the presence of sunlight and under the action of catalysts, it polymerizes to give a solid material which is used industrially as a plastic.

Vinyl bromide is a liquid (b. p. 16°) with a pleasant ethereal odour. It resembles vinyl chloride in its general chemical behaviour, and polymerizes to a white solid, insoluble in organic solvents.

105. Allyl Iodide, $\text{CH}_2=\text{CH}.\text{CH}_2\text{I}$. This compound may be obtained from allyl alcohol, or more readily from glycerol, by the action of HI or of iodine and phosphorus. In the case of glycerol,

the reaction is supposed to occur in two stages, a tri-iodide being first formed, which then loses iodine :



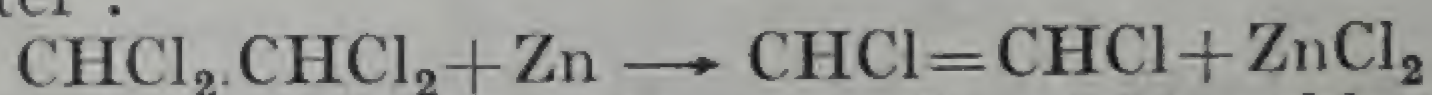
Allyl iodide is a colourless liquid (b.p. 102°) having a characteristic, mustard-like odour. It is even more reactive than alkyl halides, and readily reacts with caustic alkalies, potassium cyanide, alcoholic ammonia, and with dry magnesium. On this account, it is frequently employed in organic synthesis for the introduction of the allyl group.

Allyl chloride (b.p. 46°) and *allyl bromide* (b.p. 70°) are similar to allyl iodide.

105A. Propargyl¹ Bromide. *Propargyl Bromide*, $\text{CH}\equiv\text{C}.\text{CH}_2\text{Br}$. This is a pungent smelling liquid obtained from propargyl alcohol by the action of PBr_5 . It contains a true acetylenic function, as shown by its power to form metallic derivative, such as $\text{CCu}\equiv\text{C}.\text{CH}_2\text{Br}$. That halogen atom is in union with a singly-linked carbon atom is shown by its capacity for double decomposition.

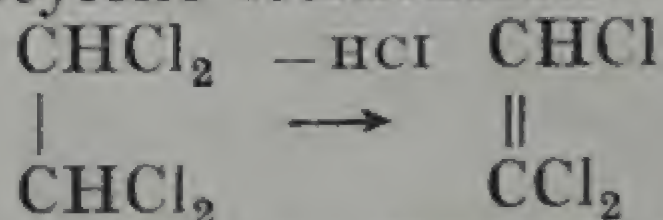
106. Di- and Trihalogen Derivatives.

Dichloro-ethylene or acetylene dichloride, $\text{CHCl}=\text{CHCl}$, is obtained by the reduction of acetylene tetrachloride by means of zinc dust and water :



Dichloro-ethylene is the best known solvent for rubber, and is used as a substitute for ether in fat extraction. It is possible to ignite the hot vapour, but the flame soon puts itself out.

Trichloro-ethylene, or Westrosol, $\text{CHCl}=\text{CCl}_2$, is obtained by heating, and stirring acetylene tetrachloride with milk of lime,



The product is submitted to steam-distillation, when trichloro-ethylene passes over.

Trichloro-ethylene is a heavy, non-inflammable liquid. It is employed on a very large scale as a solvent for fats, waxes, resins, rubber and other organic substances, and for dry-cleaning. Its low boiling-point and small latent heat render its recovery easy; there is no "after-smell," and delicate materials can be handled without fear of overheating. These facts together with its non-inflammable nature account for the gradual displacement of other solvents by trichloro-ethylene.

¹See footnote (under Sec. 94A) on page 148.

QUESTIONS

1. "The aliphatic halogen compounds are amongst the most reactive of all organic compounds."

Illustrate the statement describing some of the reactions they undergo, and the uses to which they are put in synthetic organic chemistry.

(Punjab, Inter., 1929)

2. How are methyl chloride and ethyl chloride prepared? To what uses are they put?

3. Describe in detail the preparation of ethyl bromide in the laboratory. Name as many organic compounds as you can which could be prepared from ethyl bromide as the starting material.

4. Two isomeric compounds having the composition $C_2H_4Cl_2$ are known. How are these compounds obtained, and how has their constitution been determined?

(Punjab, Inter., 1931)

5. How are the following compounds prepared, and what are they used for: (i) Ethylene bromide, (ii) carbon tetrachloride, and (iii) acetylene tetrachloride?

6. Give the preparation, tests and uses of chloroform. What precautions must be observed in storing chloroform for use as an anaesthetic? (Punjab, Inter.)

7. How would you test for chloroform in the presence of iodoform?

(Punjab, B.Sc., 1933)

8. Describe the preparation of iodoform.

(Punjab, B.Sc., 1931. Part of Question)

9. How would you prepare iodoform? Describe its properties and compare it with chloroform.

(Punjab, Inter., 1914)

10. An organic liquid containing 94.8 per cent of bromine and having a vapour density of 126.5 gave a nauseating odour on being warmed with aniline and alcoholic potash. What compound was it?

11. Into how many classes are the halogen derivatives of olefines divided? In what important respects do the members of each group differ from one another?

12. Give the preparation of allyl iodide and its use in synthetic organic chemistry?

ANSWER

10. Bromoform, $CHBr_3$.

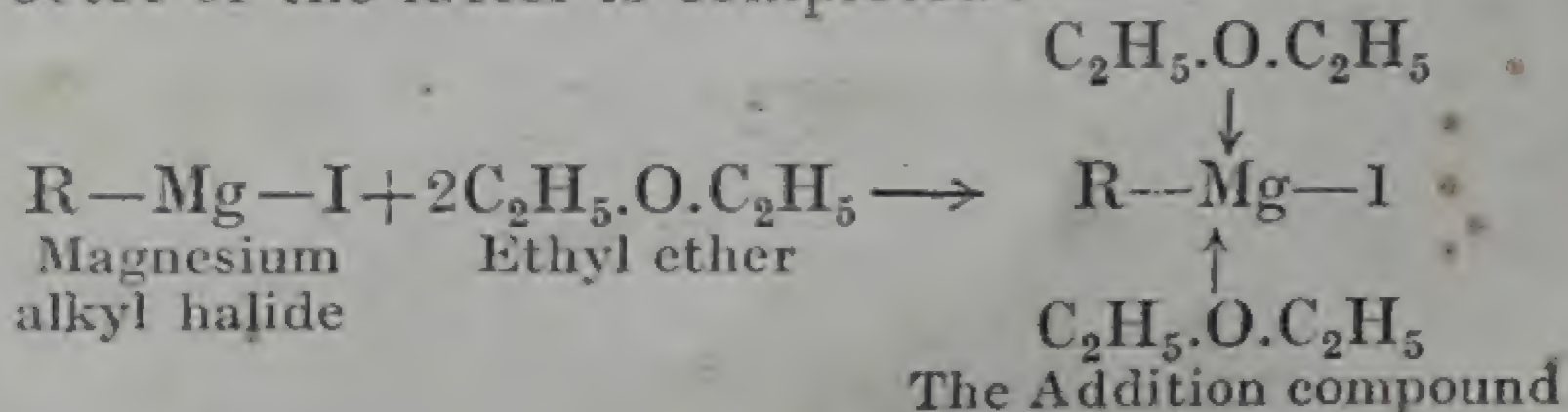
CHAPTER XIII

ORGANO-METALLIC COMPOUNDS

107. General. Alkyl halides react on certain metals, yielding derivatives called organo-metallic compounds. The most important of the organo-metallic compounds are those of magnesium and zinc. The latter were discovered by Frankland in 1849, and have been of the greatest service in the past in synthetic organic chemistry. Their place has now been taken by magnesium alkyl halides, called the *Grignard reagents*, which are less troublesome to work with, give better yields and are of far more general utility.

108. Grignard Reagents. It was shown by the French chemist Grignard, in 1903, that dry magnesium in the presence of dry ether reacts with numerous organic halogen compounds, yielding organo-magnesium halides of the type $R.Mg.Br$, which remain dissolved in the ether. He also found that the organo-magnesium halides need not be isolated for synthetic purposes, since they could be used directly in ethereal solution. They are colourless solids and, unlike Frankland's reagents, are not spontaneously inflammable in air.

Though a Grignard reagent reacts as if it were simply a magnesium alkyl halide, there is no doubt that it exists in combination with ether. In the ether molecule, there are two lone pairs of electrons on the oxygen atom, one of which is usually effective, and is, in this case, donated to the magnesium atom. The combination occurs between *two* ether molecules with a molecule of magnesium alkyl halide. The two lone pairs of electrons from the two ether molecules are donated to the magnesium atom (which has only four valency electrons), whereby the octet of the latter is completed:—



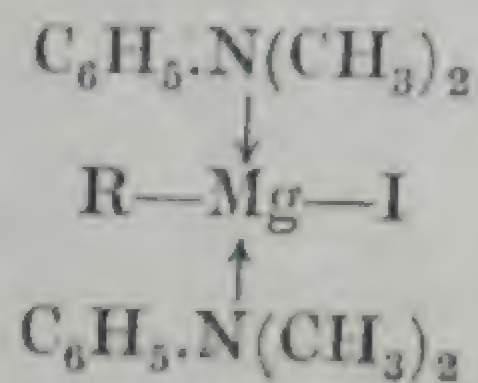
Anisole (phenyl methyl ether, $C_6H_5.O.CH_3$), and dimethyl aniline, $C_6H_5.N(CH_3)_2$, may also be used in the Grignard reaction in place of ether. The co-ordination of the first compound with magnesium

VICTOR GRIGNARD
(1871—1935)

was Professor of Chemistry at the University of Lyons, France. In 1912, he was awarded the Nobel Prize for his discovery of Magnesium Alkyl Halides which have proved of inestimable value in the synthesis of a large variety of organic compounds.



alkyl halide occurs through the lone pair of electrons on the oxygen atom exactly as in diethyl ether. In the case of the latter compound, it occurs through the lone pair of electrons on the nitrogen atom, as shown below:—



108A. Preparation of Grignard Reagents. A Grignard reagent is formed with development of heat, when a halogen derivative of an aliphatic or aromatic hydrocarbon (1 mol.) is added to metallic

magnesium (1 gram-atom) in the presence of pure dry ether. The metal gradually disappears, and on evaporating the solution, colourless, hygroscopic crystals separate out. These consist of a Grignard reagent in combination with two molecules of ether.

For use in various syntheses, it is, however, not necessary to isolate the crystalline compound. Hence, in actual practice, an *ethereal solution* of the Grignard reagent is prepared and used as such.

Expt. 37. Preparation of Methyl Magnesium Iodide. In this preparation, the reagents used must be *thoroughly dry*. Magnesium, in the form of powder, is dried in an oven at $110-120^{\circ}$ for 3 hours. Methyl iodide is allowed to stand for some time over fused calcium chloride and then redistilled. The ether is purified by shaking several times with *small* amounts of water in order to remove alcohol, and then dried by letting it stand successively over freshly fused calcium chloride and metallic sodium, and finally distilled over phosphorus pentoxide.

In a clean, dry round-bottom flask of 250 c.c. capacity, provided with a reflux condenser and a dropping funnel (both previously dried) place 3 grams of dry magnesium powder and cover this with 50 c.c. of dry ether. Set up the apparatus on a cold water bath, fit the upper end of the condenser with a calcium chloride tube, and place in the dropping funnel a solution of 8 c.c. of dry methyl iodide in dry ether. Let a few drops of the solution fall into the flask. If the reaction does not set in spontaneously within 5 minutes, a flake of iodine is added and the flask gently warmed. Once the reaction has begun, it is only necessary to continue the addition of methyl iodide solution at such a rate that the reaction does not become too violent. When all the methyl iodide solution has been added, the mixture is heated on the water bath, until the magnesium has completely disappeared.

108B. Reactions and Synthetic Uses of Grignard Reagents. Grignard reagents have attained a position in synthetic organic chemistry unrivalled by any other class of compounds. With the aid of these reagents, it is possible to synthesize a large variety of organic substances. The reactions of Grignard reagents may be divided into three groups: (1) double decompositions, (2) addition reactions, and (3) reactions involving both double decomposition and addition. In studying these reactions, it may be remembered:

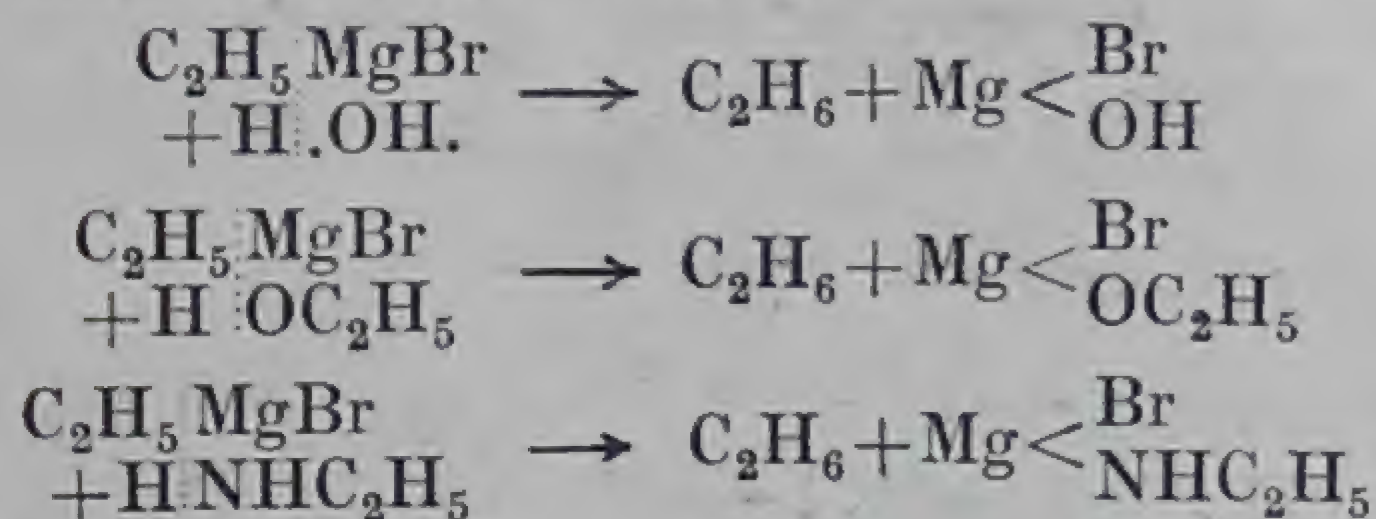
(a) that *magnesium has a great affinity for oxygen and other electronegative atoms and groups, and*

(b) that *the bond between magnesium and carbon is readily broken.*

(1) **Double decompositions.** These involve the removal of the *electropositive* group,—MgBr, of the Grignard reagent together with the *electronegative* part of the reacting molecule, the remaining parts of the two molecules combining together to give a new product. The following are the important examples of reactions of this class:—

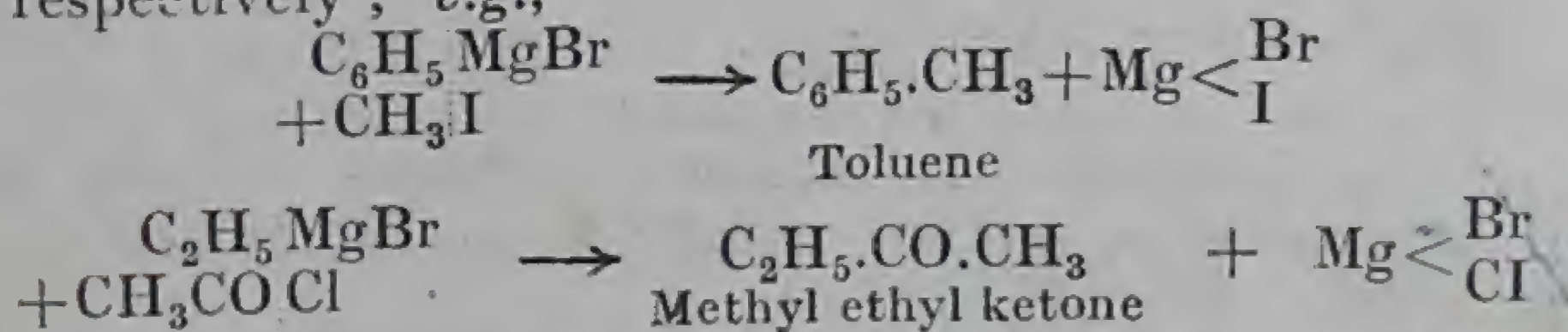
(i) **Reaction with Compounds containing Active Hydrogen.** Grignard reagents undergo double decomposition with certain compounds

containing active hydrogen, *e.g.*, water, alcohols, thio-alcohols, primary and secondary amines, etc., yielding *hydrocarbons*.

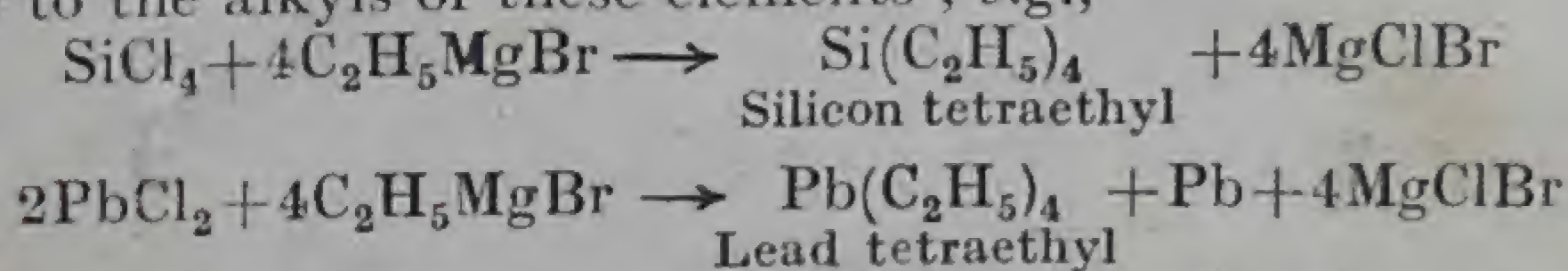


The action of a Grignard reagent (*e.g.*, methyl magnesium iodide or ethyl magnesium bromide) on compounds containing active hydrogen is employed for the *detection* and *estimation* of such substances. In the latter case, the volume of methane or ethane evolved is measured.

(ii) *Reaction with Halogen Compounds.* Alkyl halides and acid chlorides react with Grignard reagents, yielding *hydrocarbons* and *ketones* respectively; *e.g.*,

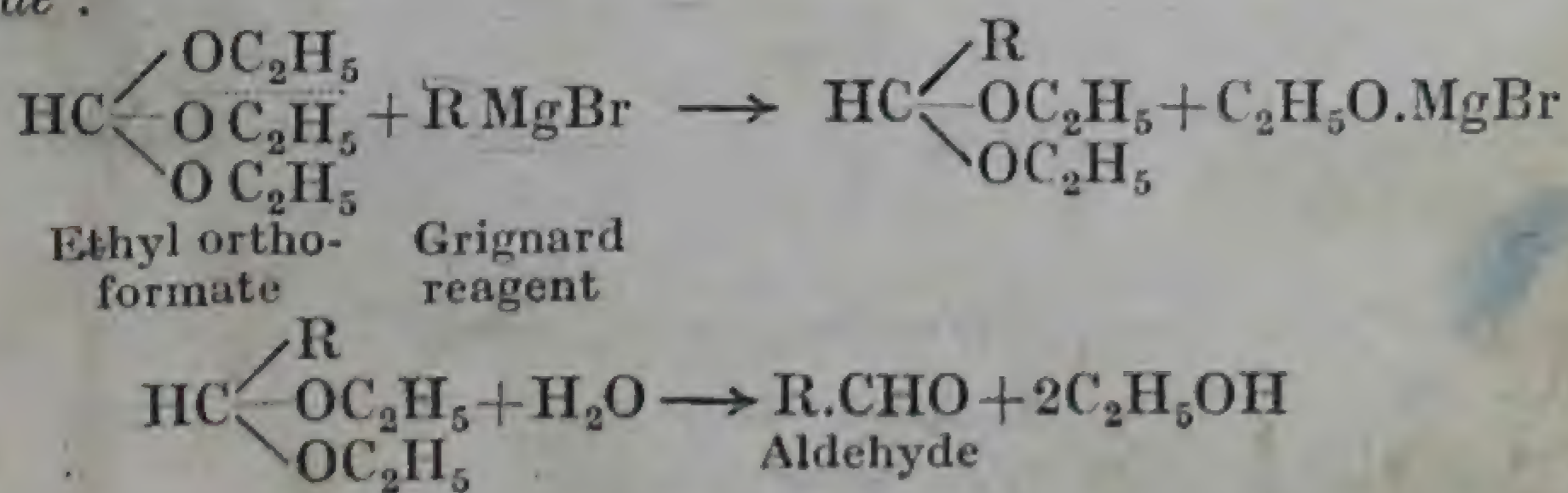


Halides of certain metals and non-metals (*e.g.*, Hg, Si, Sn, Pb, etc.) give rise to the alkyls of these elements; *e.g.*,



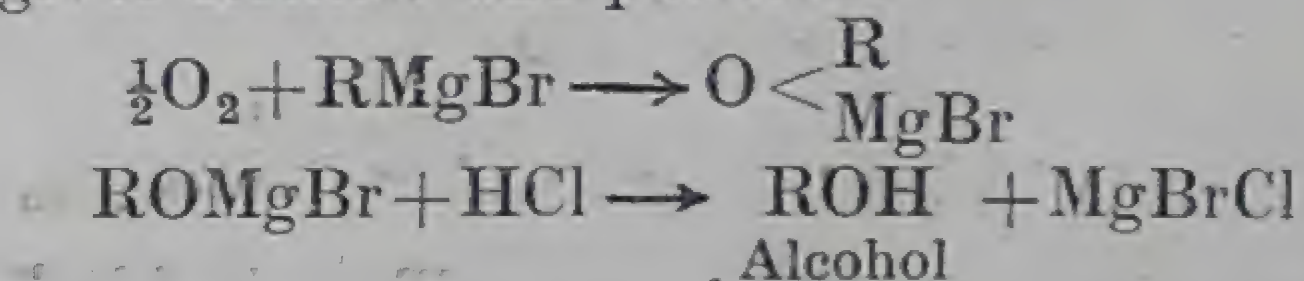
In the case of lead, there occurs an increase of valency with the liberation of one-half of lead.

(iii) *Reaction with Ethyl Orthoformate.* Ethyl orthoformate exchanges one ethoxy group for the alkyl radical of the reagent. The product is decomposed by water or a dilute acid, yielding an *aldehyde*:

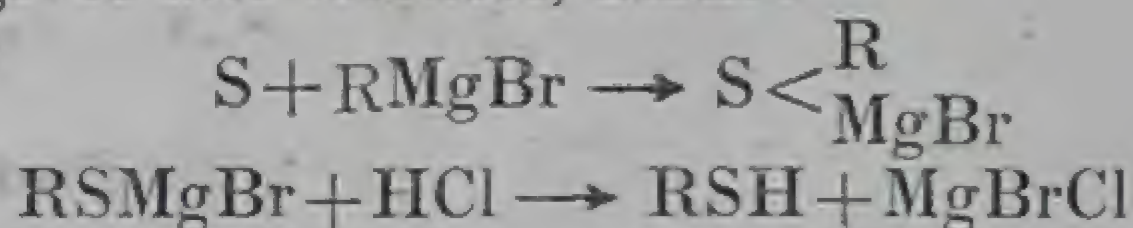


(2) **Addition Reactions.** Grignard reagents have a great tendency to directly combine with oxygen, sulphur, and compounds containing unsaturated groups to give addition products, which are readily decomposed by dilute hydrochloric acid, giving alcohols and other compounds :—

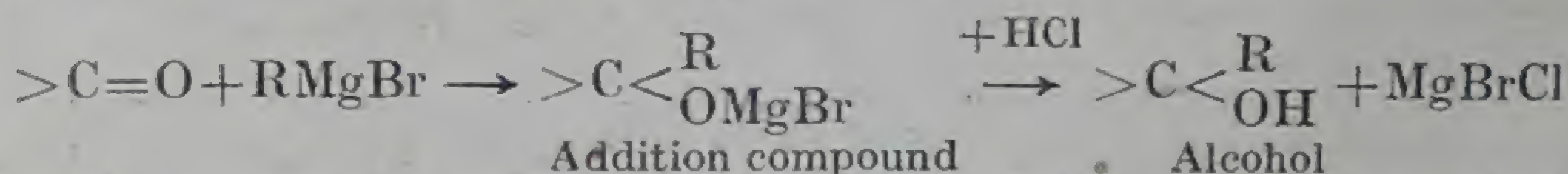
(i) Oxygen gives *alcohols* and *phenols* :



(ii) Sulphur gives *thio-alcohols*, RSH :

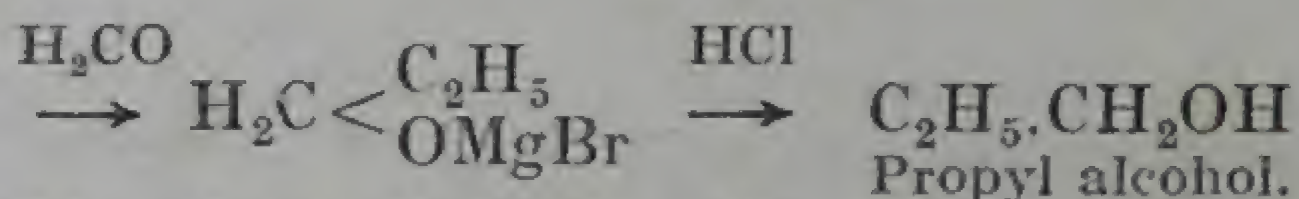
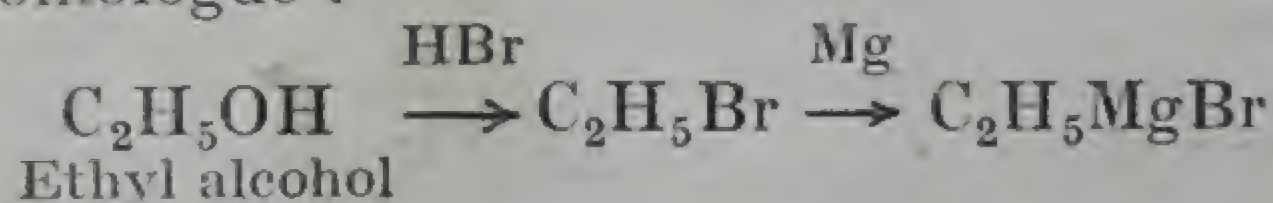


(iii) Aldehydes and ketones give *alcohols* :

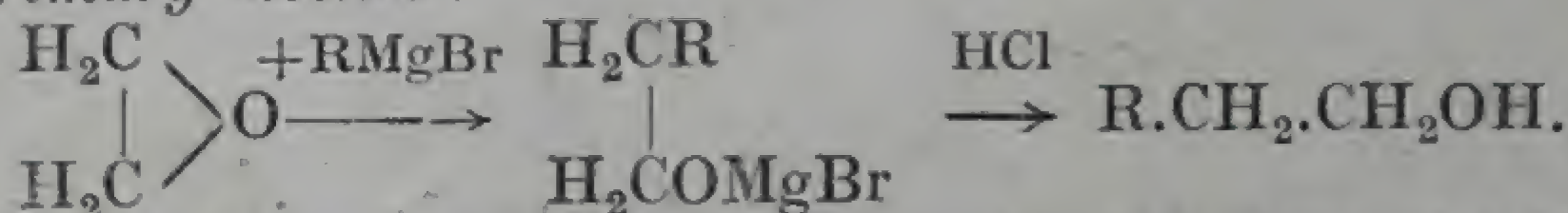


By this means, formaldehyde, $\text{H}_2\text{C}=\text{O}$, yields a *primary* alcohol, $\text{R}.\text{CH}_2\text{OH}$, other aldehydes gives *secondary* alcohols, R_2CHOH , while ketones give *tertiary* alcohol, R_3COH .

The reaction with formaldehyde may be used for ascending a homologous series, *i.e.*, preparing a higher alcohol from a lower homologue :

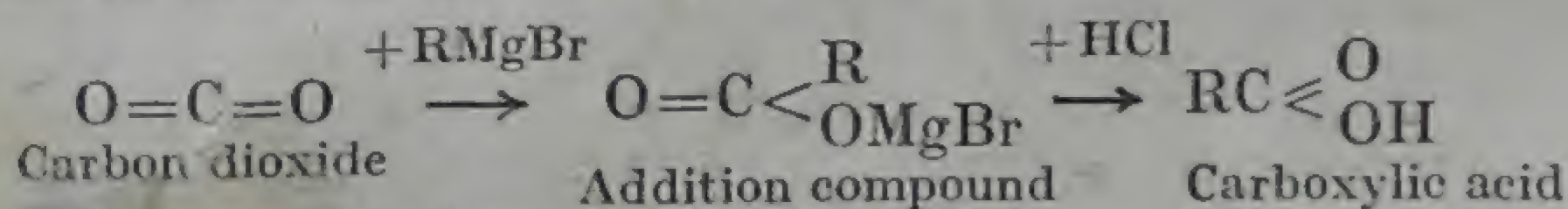


(iv) Ethylene oxide reacts like formaldehyde, the final product being a *primary* alcohol :



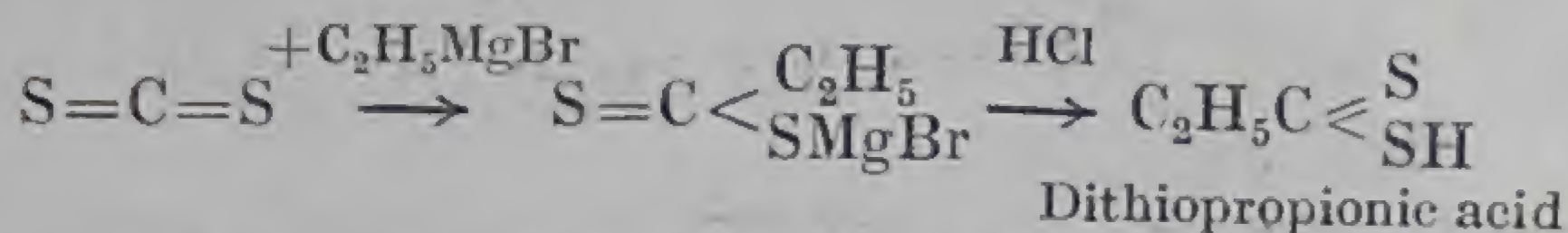
This reaction helps up in ascending a series *two steps at a time*.

(v) Carbon dioxide gives a *carboxylic acid* :

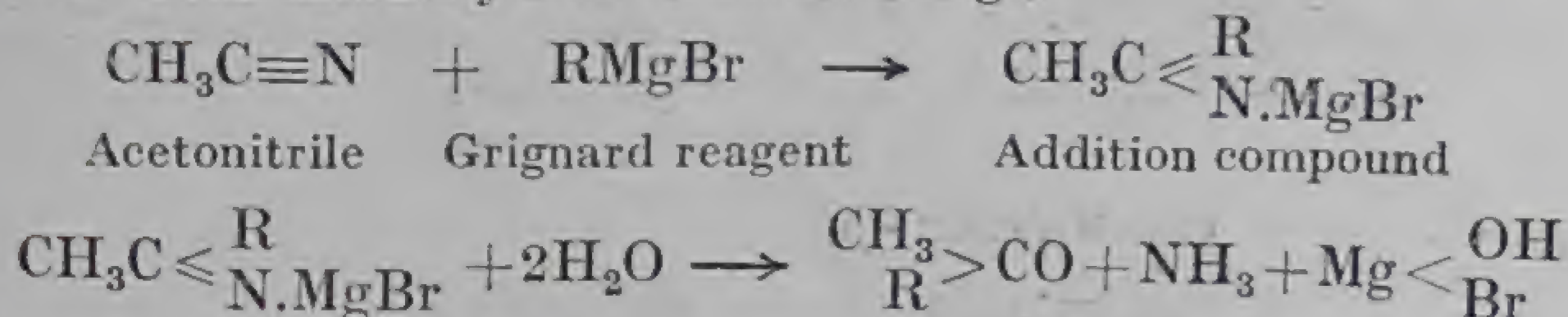


This reaction also lengthens the carbon-chain.

(vi) Similarly, carbon disulphide gives a dithio-carboxylic acid ;
e.g.,

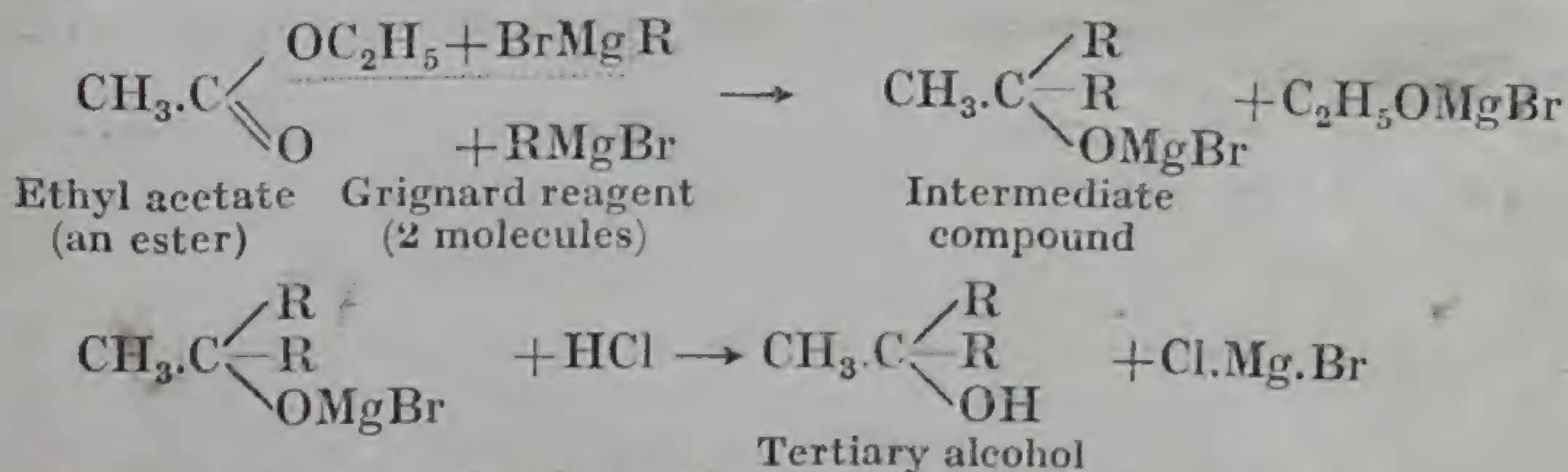


(vii) An acid nitrile yields a *ketone* ; e.g.,



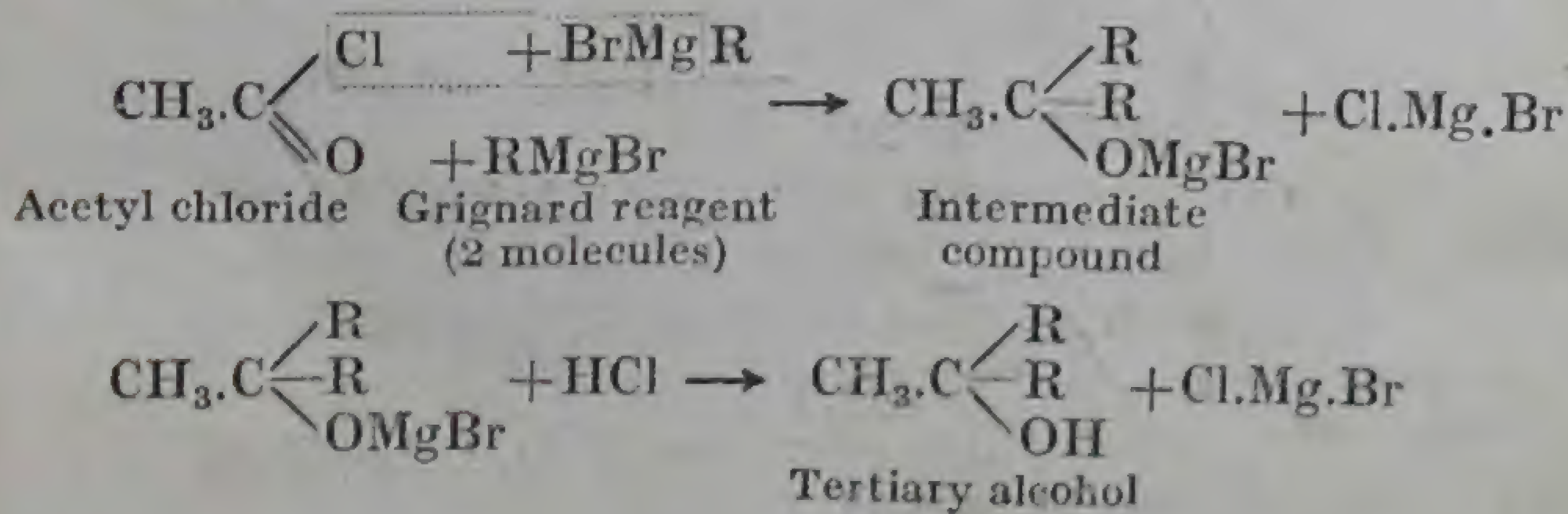
(3) Reactions involving both Double Decomposition and Addition. In these cases, *two* molecules of the Grignard reagent are used up, one for double decomposition and the other for addition. The following are the more important examples of such reactions :—

(i) An ester (other than a formate) yields a *tertiary alcohol*, in which one of the alkyl groups is derived from the acid component of the ester and two from the Grignard reagent.

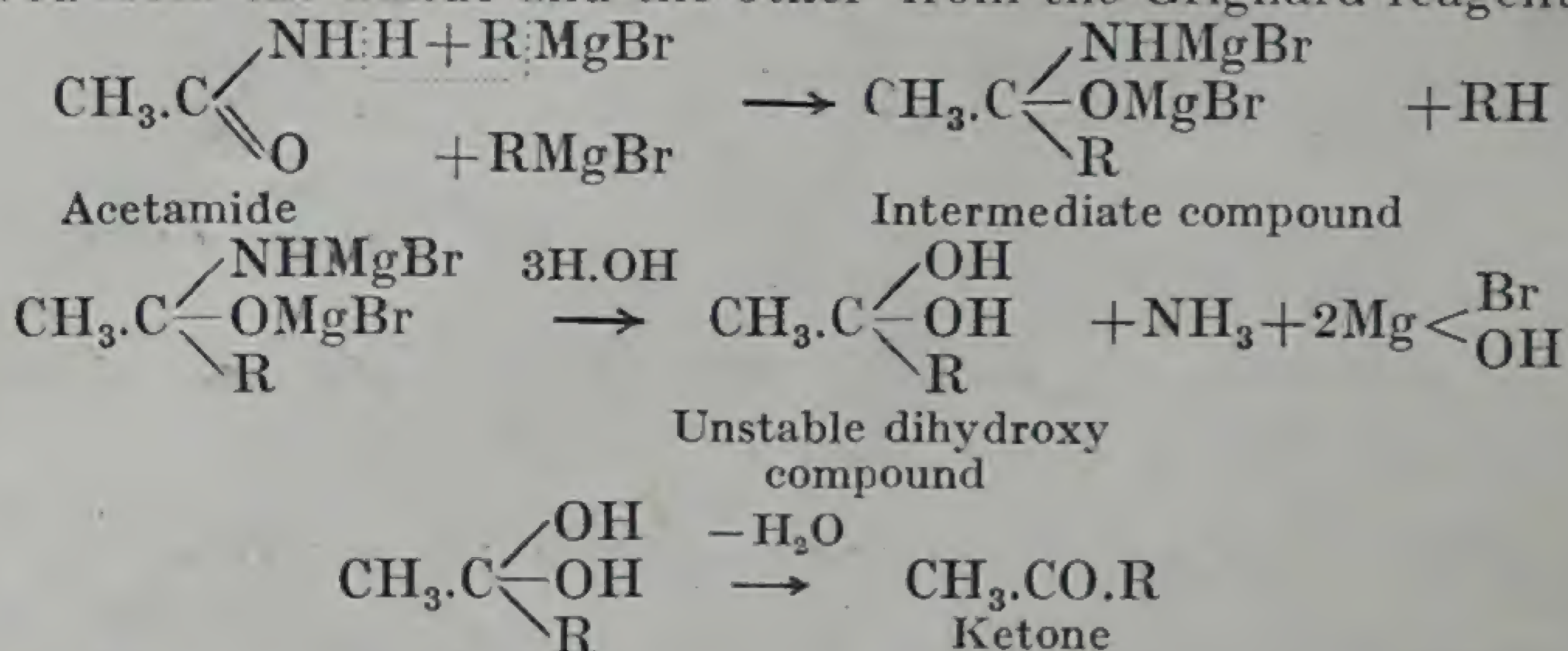


Formic esters lead to the formation of *secondary alcohols*.

(ii) An acid chloride reacts in the same manner as an ester, the final product, is a *tertiary alcohol* :—



(iii) an **amide** gives a *ketone* in which one of the alkyl groups is derived from the amide and the other from the Grignard reagent :—

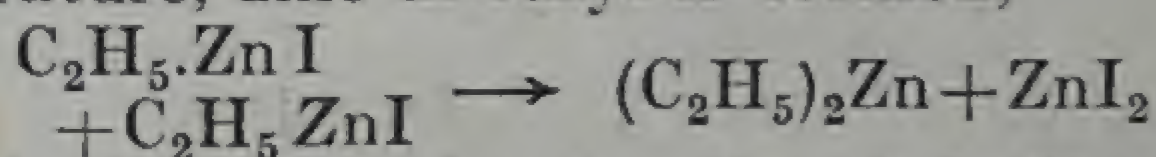


109. Zinc Alkyls. As already mentioned, zinc alkyls were discovered by Frankland in 1849. A typical example of this class of compounds is *zinc ethyl*, the preparation and properties of which are described below.

Zinc Di-ethyl, $\text{Zn}(\text{C}_2\text{H}_5)_2$, is prepared by heating zinc filings with ethyl iodide in an atmosphere of carbon dioxide. The reaction proceeds in two stages : the first product is a colourless solid (*zinc ethyl iodide*),



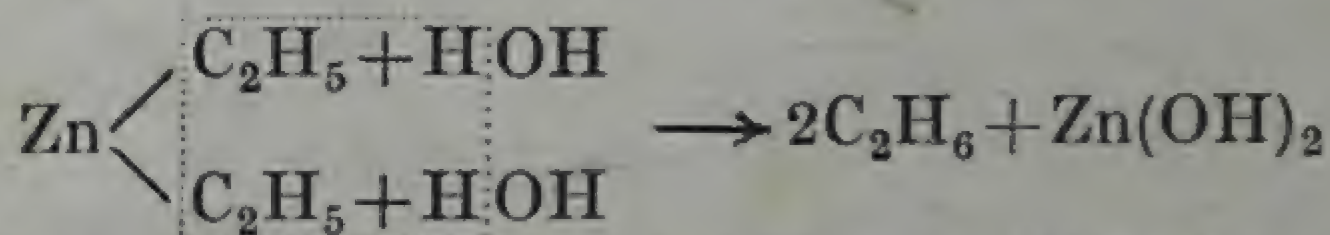
on raising the temperature, zinc di-ethyl is formed,



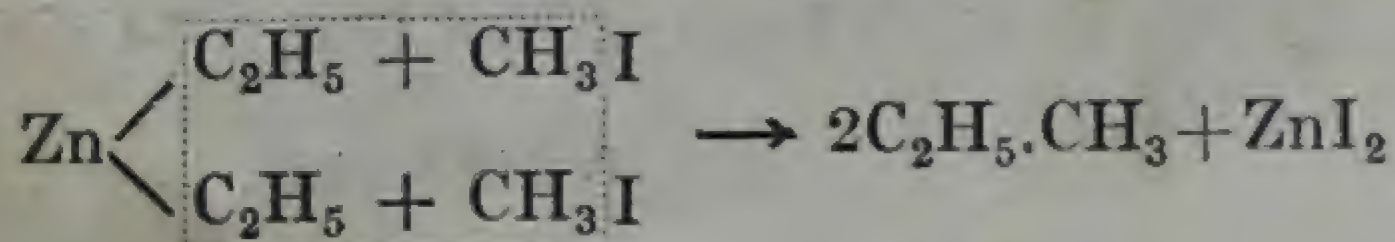
Properties. Zinc di-ethyl is a colourless liquid, boiling at 118° . It is spontaneously inflammable in air, and burns with a bright flame and a characteristic greenish colour, which gives off zinc oxide fumes.

The reactions of zinc di-ethyl are as follows :—

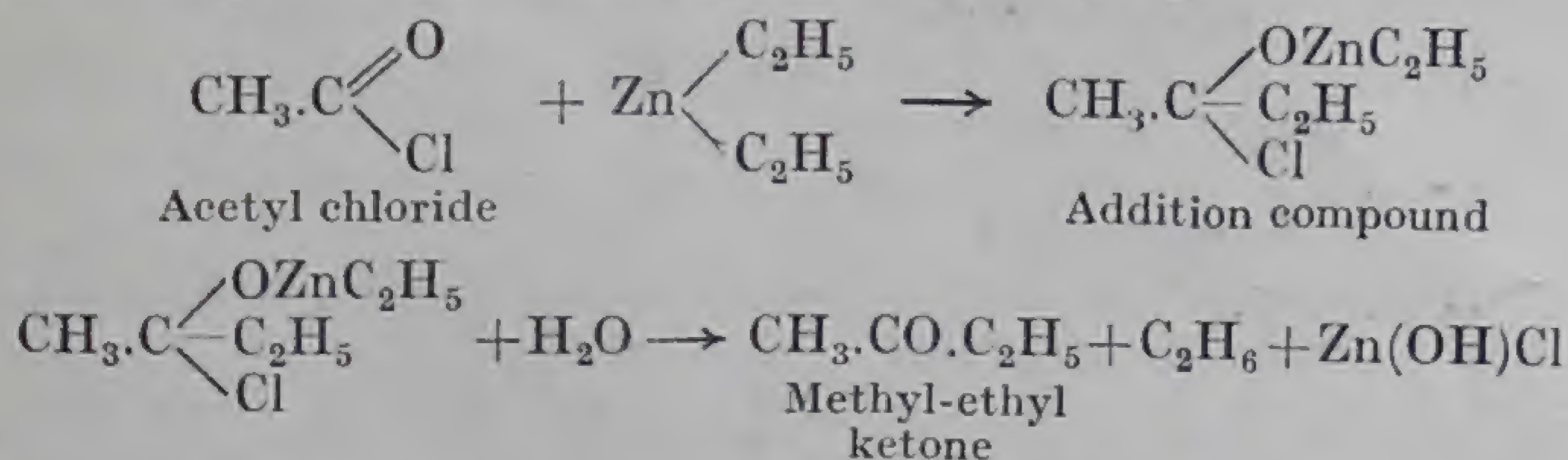
(1) It is readily decomposed by *water*, *alcohol*, and other compounds containing a hydroxyl group, *ethane* being produced.



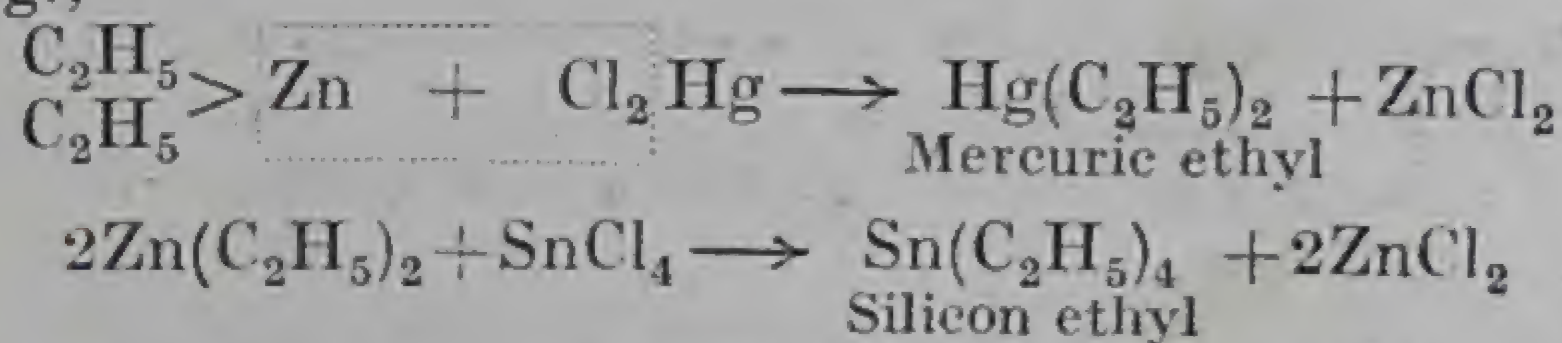
(2) It reacts with almost all *halogen compounds*, whether organic, or inorganic. Thus, with an *alkyl halide*, a hydrocarbon is produced



With an *acid chloride*, an additive product is formed, which, on being decomposed with water, yields a *ketone*; *e.g.*,



When zinc di-ethyl is treated with chlorides of certain metals and non-metals, the ethyl group is transferred from zinc to the other element; *e.g.*,



110. Lead Tetra-ethyl, $\text{Pb}(\text{C}_2\text{H}_5)_4$. Besides magnesium and zinc, certain other metals form alkyl compounds. The most important of these is lead tetra-ethyl, which is prepared from ethyl magnesium bromide as given on page 167. It is an essential constituent of anti-knock fuels, capable of burning smoothly under high compression, (see foot-note, page 131).

QUESTIONS

1. Give a general account of the organo-metallic compounds. In what ways have they been used in organic synthesis? (*Punjab, B.Sc., Hons., 1926*)
2. Give the preparation and synthetic uses of Grignard reagents. (*Punjab, B.Sc., Hons., 1927; 1931*)
3. How is magnesium ethyl bromide prepared in ethereal solution? Give equations to illustrate the use of this compound in the formation of (a) hydrocarbon, (b) a carboxylic acid, (c) a secondary alcohol, and (d) an alkyl derivative of a metal. (*Punjab, B.Sc., 1934*)
4. 0.1140 gm. of a thio-alcohol, RSH , on being added to an excess of an ethereal solution of ethyl magnesium bromide, caused the evolution of 44.5 c.c. of ethane measured at 20° and 735 mm. Calculate the molecular weight of the thio-alcohol.
5. 0.4328 gm. of a mixture of ethyl alcohol and ether when treated with an excess of methyl magnesium iodide gave 48.33 c.c. of methane measured at 20° and 755 mm. Calculate the percentage of alcohol in the mixture.
6. Give the preparation and synthetic uses of zinc alkyls.
7. Write an essay on organo-metallic compounds and their applications. (*Punjab, B.Sc., 1941*)

ANSWERS

4. 62.

5. 21.2%.

CHAPTER XIV

MONOHYDRIC ALCOHOLS

111. General. Monohydric alcohols are derived from aliphatic hydrocarbons by the replacement of a hydrogen atom by a hydroxyl group. The most important series is that derived from paraffin hydrocarbons, and possesses the general formula, $C_nH_{2n+1}OH$, or $C_nH_{2n+2}O$.

Classification. Monohydric alcohols are divided into three classes, *primary*, *secondary* and *tertiary*, according as they contain the group $-CH_2OH$, $>CHOH$, or >COH . The three classes are distinguished from one another by (i) behaviour on oxidation, (ii) behaviour towards hot, reduced copper, and (iii) behaviour of the corresponding nitro-paraffins towards nitrous acid (see Sec. 115).

Nomenclature. Alcohols are usually named after the alkyl group that they contain. The Geneva names are derived from those of the hydrocarbons by changing the terminal *-e* into *-ol*. A third method consists in regarding them as derivatives of methyl alcohol, CH_3OH , or carbinol as it is termed in this connection.

$CH_3.OH$
Methyl alcohol
methanol, or carbinol

$CH_3.CH_2OH$
Ethyl alcohol, ethanol,
or methyl carbinol

$CH_2=CH.CH_2OH$
Allyl alcohol, 1-propene 3-ol, or vinyl carbinol.

Isomerism. The structural isomerism among alcohols may be due to (i) differences in the linking of carbon chain, (ii) the difference in position of the hydroxyl group in the molecule, or (iii) both these at the same time. An alcohol which is derived from a normal hydrocarbon is termed a *normal* alcohol.

Methyl and ethyl alcohols occur only in one form. There are two propyl alcohols, one primary and the other secondary.

(1) $CH_3.CH_2.CH_2OH$

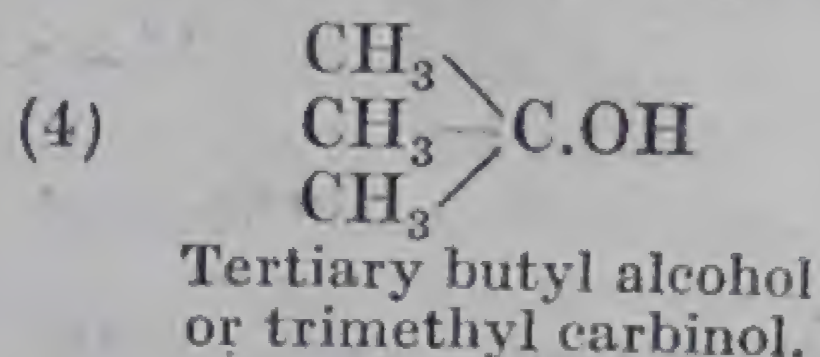
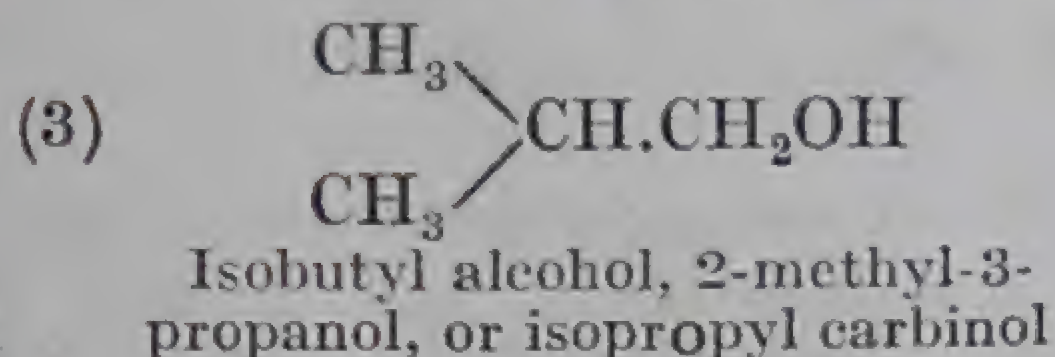
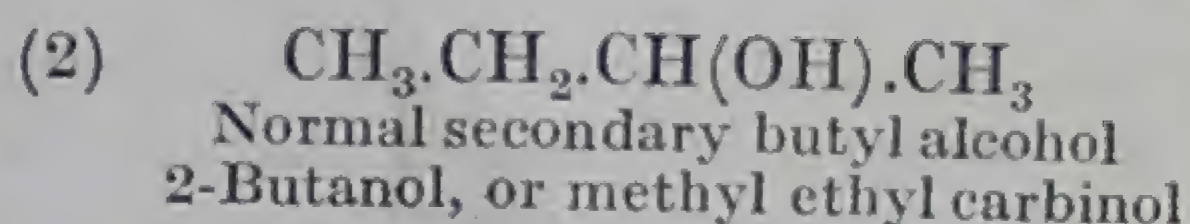
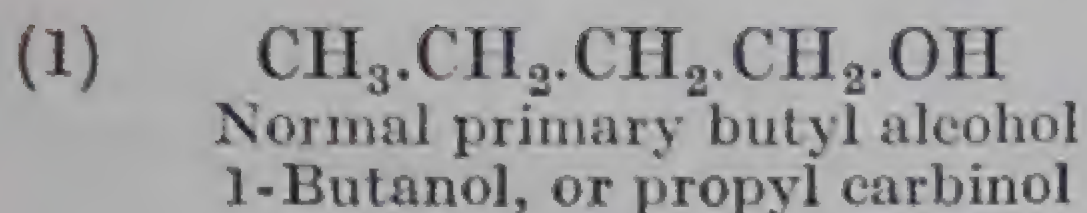
Normal propyl alcohol

1-propanol, or ethyl carbinol

(2) $CH_3.CH(OH).CH_3$

Isopropyl alcohol, 2-propanol
or dimethyl-carbinol

and four butyl alcohols, two derived from normal butane (1 and 2) and two from isobutane (3 and 4),



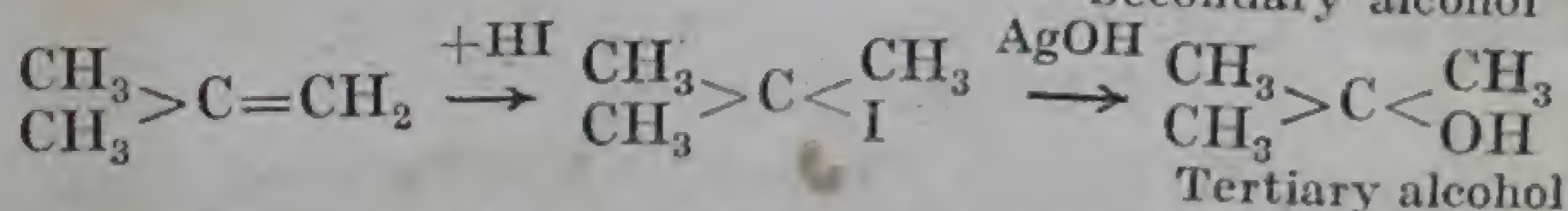
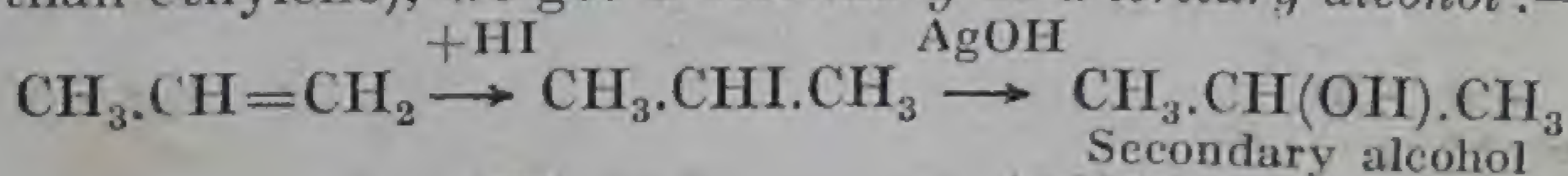
SATURATED MONOHYDRIC ALCOHOLS

112. Methods of Formation. Monohydric alcohols derived from saturated hydrocarbons can be obtained by the following general methods:—

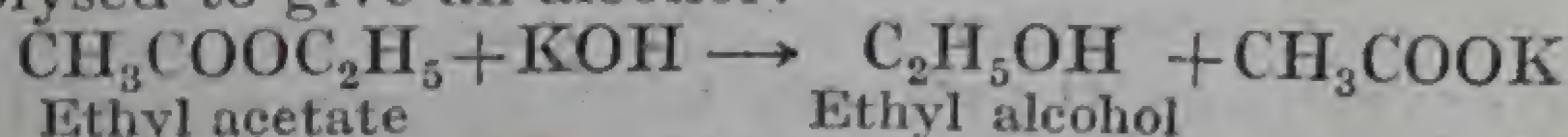
(1) *By Hydrolysis of Alkyl Halides.* When an alkyl halide is brought into contact with silver hydroxide or boiled with an aqueous solution of an alkali hydroxide, it is converted into alcohol:



Since the alkyl halides can be obtained from *paraffin hydrocarbons* by substitution, and also from the *olefines* by the addition of a halogen acid, the aliphatic alcohols may be indirectly produced from these hydrocarbons. In the case of olefines, the addition of the halogen acid always occurs in such a manner that the halogen atom gets attached to that carbon atom which carries the *smaller* number of hydrogen atoms (Sec. 85). Hence, if we start with an olefine (other than ethylene), we get a *secondary* or a *tertiary alcohol*:—

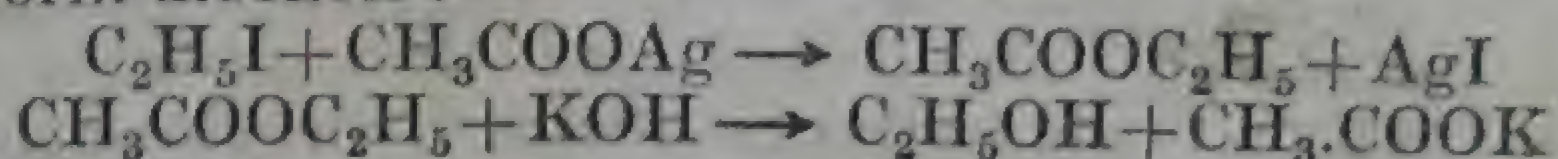


(2) *By Hydrolysis of Esters.* When an ester is boiled with an alkali, it is hydrolysed to give an alcohol:—



The method is chiefly employed for preparing certain *higher alcohols* present in ethereal oils and waxes occurring in nature. The preparation of glycerol from fats and oils is another important example.

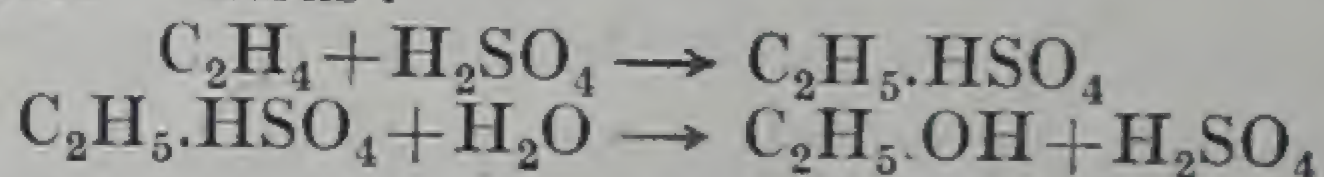
An indirect application of this method is based on the fact that *alkyl halides*, when heated with silver acetate or potassium acetate, give rise to alkyl acetates. These latter, on being boiled with alkali solutions, form alcohols:—



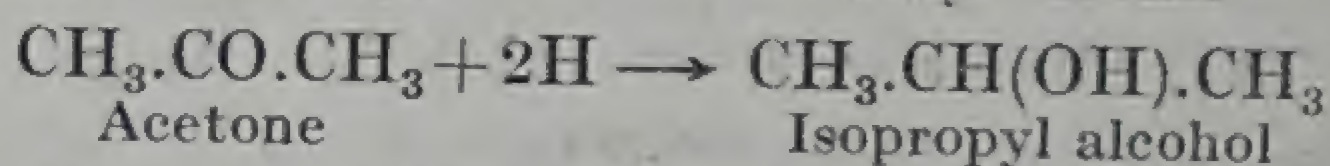
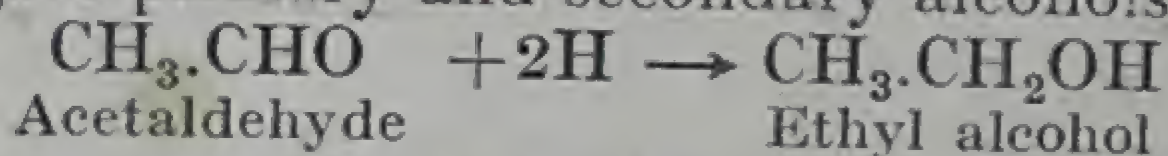
This method is much used in the preparation of higher alcohols since the higher alkyl halides (*e.g.*, hexyl chloride), on direct treatment with alkalis, give rise mainly to olefines,

$\text{CH}_3.(\text{CH}_2)_3.\text{CH}_2.\text{CH}_2\text{Cl} + \text{KOH} \longrightarrow \text{CH}_3.(\text{CH}_2)_3.\text{CH}=\text{CH}_2 + \text{KCl} + \text{H}_2\text{O}$,
the yield of alcohol being very small.

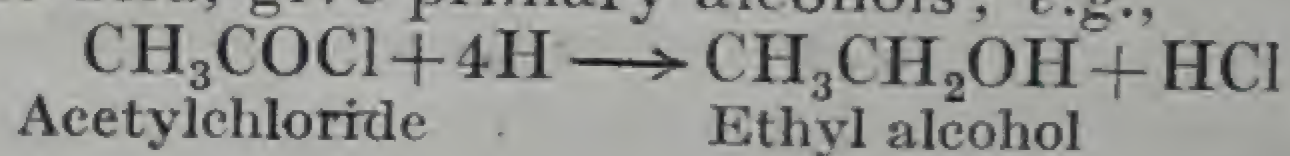
Another application of the same method consists in dissolving an *olefine hydrocarbon* in concentrated sulphuric acid and boiling the solution with water. Thus:



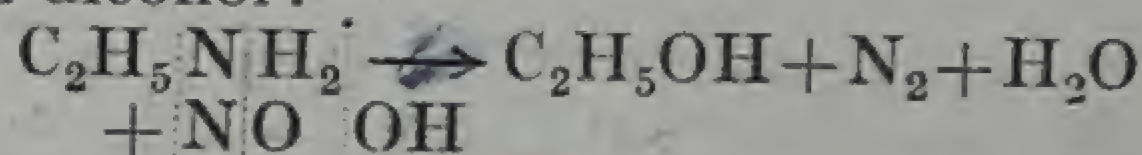
(3) *By Reduction of Aldehydes and Ketones.* Aldehydes and ketones, on reduction with nascent hydrogen (sodium amalgam and very dilute sulphuric acid), give primary and secondary alcohols respectively:—



(4) *By Reduction of Acid Chlorides or Anhydrides.* These compounds on being reduced by means of sodium amalgam and very dilute sulphuric acid, give primary alcohols; *e.g.*,

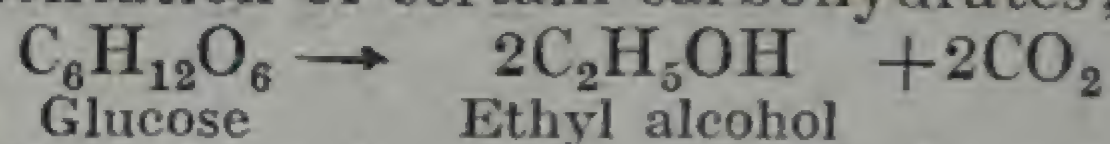


(5) *By Action of Nitrous Acid on Primary Amines.* When a primary amine is treated with nitrous acid ($\text{NaNO}_2 + \text{HCl}$), the NH_2 group gets replaced by an OH group, and an alcohol is produced. Thus ethylamine gives ethyl alcohol:—



(6) *By Means of Grignard's Reagents.* Grignard's reagents combine with aldehydes, ketones, ethylene oxide, esters and acid chlorides, giving addition products, which, on treatment with a dilute mineral acid, yield primary, secondary and tertiary alcohols (Sec. 108). They also absorb oxygen and the product when decomposed with water or a dilute acid yields an alcohol (Sec. 108).

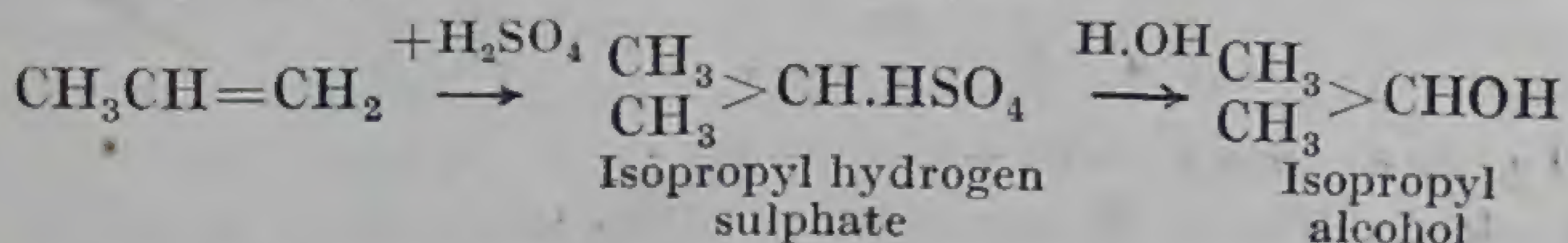
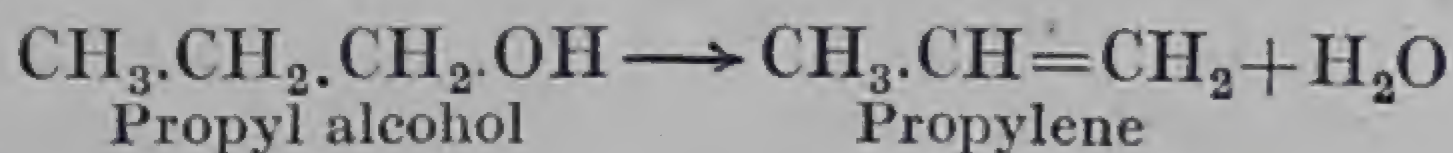
(7) By the fermentation of certain carbohydrates; *e.g.*,



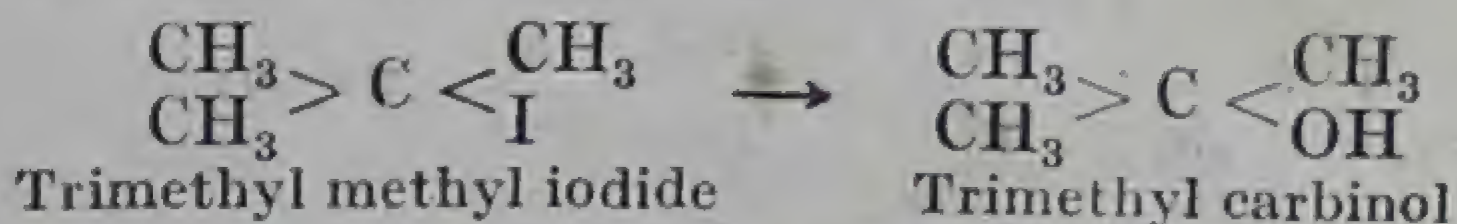
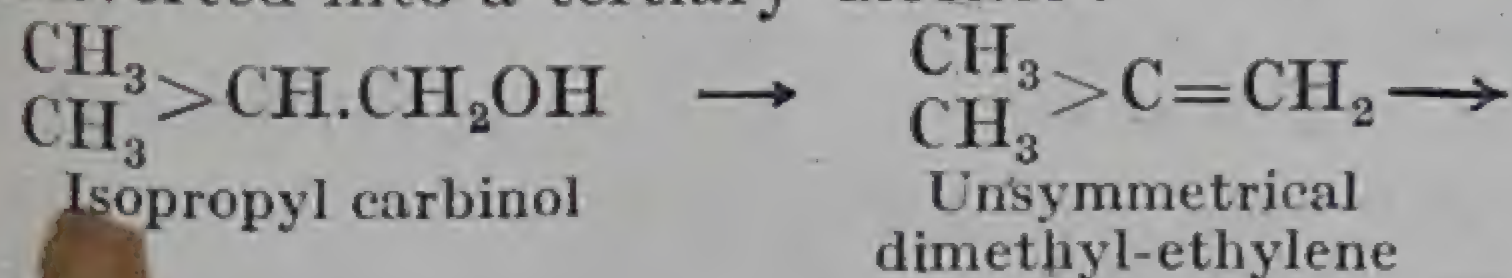
This method, though not very general, is of great commercial importance.

113. Conversion of Primary into Secondary and Tertiary Alcohols. This is effected through an olefine hydrocarbon, which is then made to combine with hydriodic acid or fuming

sulphuric acid, the acidic group in either case attaching itself to the less hydrogenated carbon atom (Markownikoff's rule Sec. 83). The resulting ester is then hydrolysed, in the first case, by boiling with an aqueous solution of caustic soda, and in the second, by diluting with water and boiling. Thus, propyl alcohol may be converted into isopropyl alcohol as shown below :



Similarly, a primary alcohol, such as isopropyl carbinol, may be converted into a tertiary alcohol :



114. Properties. *Physical.* Most of the alcohols derived from hydrocarbons up to C_{12} are colourless liquids at ordinary temperatures. Trimethyl carbinol, $(\text{CH}_3)_3\text{COH}$, and the higher members (*e.g.*, cetyl alcohol, $\text{C}_{16}\text{H}_{33}\cdot\text{OH}$, and melissyl alcohol, $\text{C}_{30}\text{H}_{61}\cdot\text{OH}$, which occur as palmitates in spermaceti and beeswax respectively) are solids. The lower members possess a characteristic alcoholic smell and taste, the intermediate ones have an unpleasant odour, while the higher homologues are tasteless and odourless.

In most of the organic solvents, the alcohols are miscible in all proportions. The first three members are soluble in water, but with the higher members the solubility rapidly decreases. Thus amyl alcohols are only sparingly soluble in water. The solvent power of alcohols for inorganic salts also decreases with the increasing number of carbon atoms. This will be clear from the following table, in which number of grams of each salt dissolved by 100 grams of the alcohol at 25° are given :

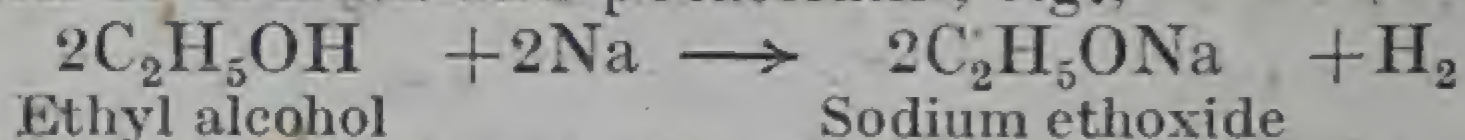
Salt	Water	Methanol	Ethanol	Propanol
KCl	39.9	0.53	0.022	0.004
KBr	67.7	2.17	0.142	0.035
KI	148.3	18.04	2.16	0.43

For alcohols of similar structure, the boiling point rises regularly with the increasing molecular weight, there being a rise of about 20° for each increment of one carbon atom. Among isomeric alcohols, the boiling-point decreases with a shifting of the hydroxyl group towards the centre of the chain, shifting of this group by one carbon atom towards the centre causing a decrease of about 15° . Primary alcohols, therefore, boil at higher temperature than the corresponding secondary alcohols, and the latter at higher temperatures than the corresponding tertiary compounds (See under propyl alcohols and butyl alcohols). The specific gravity increases with the rising molecular weight, but is in all cases less than one.

Chemical. The reactions of an alcohol involve the hydroxyl group present in the molecule, and may be divided into the following two groups :—

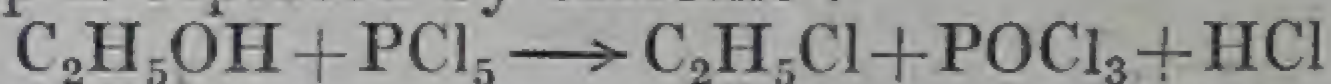
(1) *Reactions involving only the Hydroxyl Group :*

(i) The hydrogen of the hydroxyl group in an alcohol is replaceable by *metals* such as sodium and potassium ; *e.g.*,

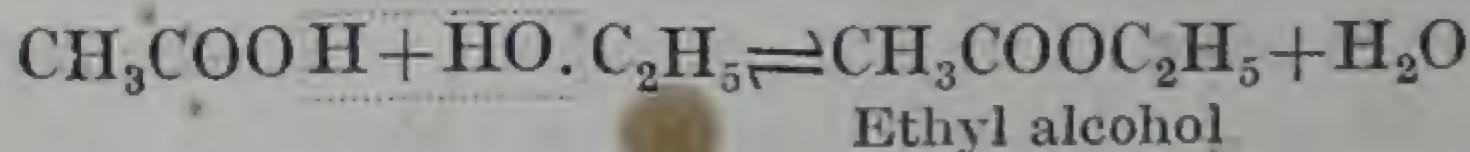


(ii) The alcohols also react with Grignard's reagents, the hydrogen of the hydroxyl group going to the alkyl group of a Grignard reagent with the production of a hydrocarbon (see Sec. 108).

(iii) When an alcohol is treated with *phosphorus pentachloride*, the hydroxyl group is replaced by chlorine :

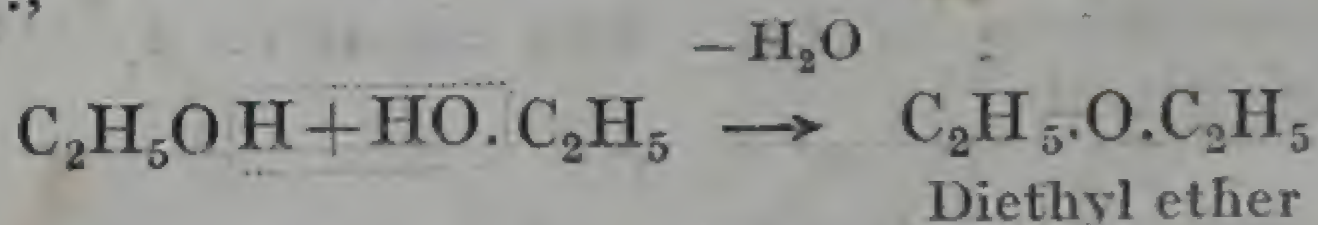


(iv) Being basic in nature, alcohols react with acids¹, yielding esters :



Expt. 38. Take a few drops each of ethyl alcohol and glacial acetic acid in a tube, add a small quantity of concentrated sulphuric acid, and warm the mixture : pleasant fruity odour.

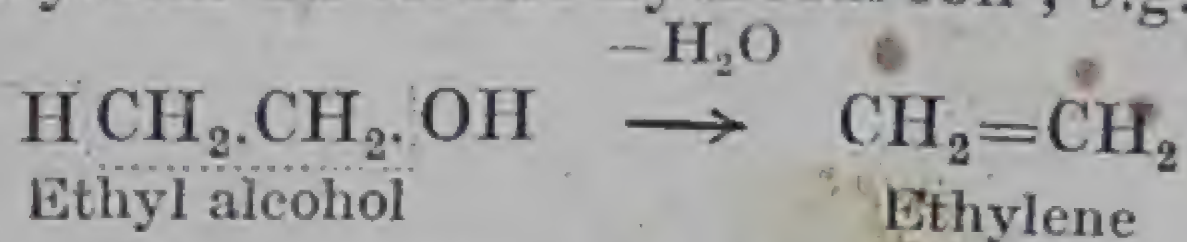
(v) In the presence of concentrated sulphuric acid, two molecules of an alcohol combine together, with the elimination of water, *ether* being produced ; *e.g.*,



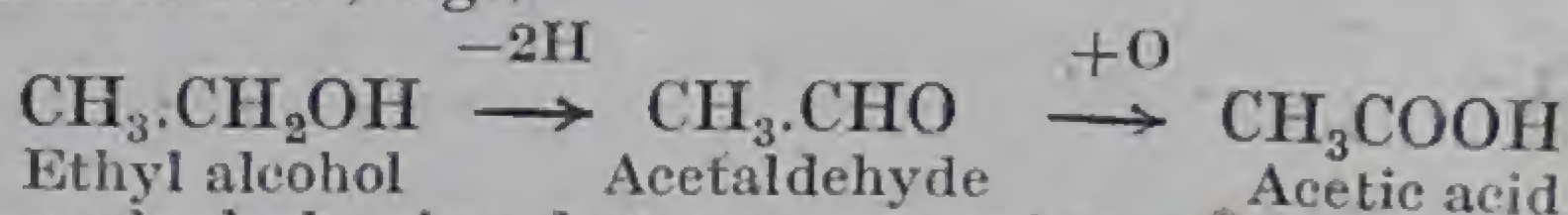
(2) *Reactions involving the Hydroxyl Group and Another Part of the Molecule (intramolecular reactions) :—*

¹ Esters are also formed with acid chlorides and anhydrides (q. v.).

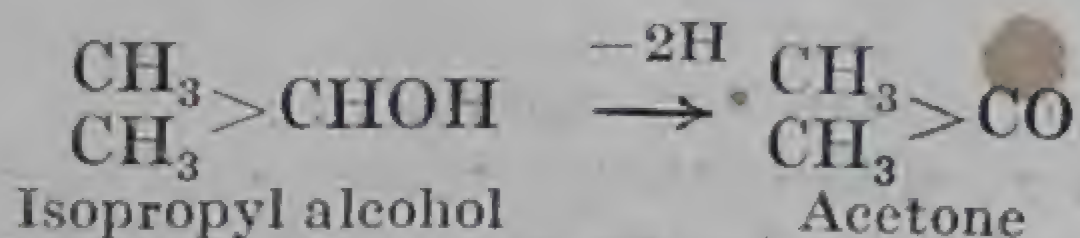
(i) When heated strongly with an excess of concentrated sulphuric acid, an alcohol yields an olefine hydrocarbon ; *e.g.*,



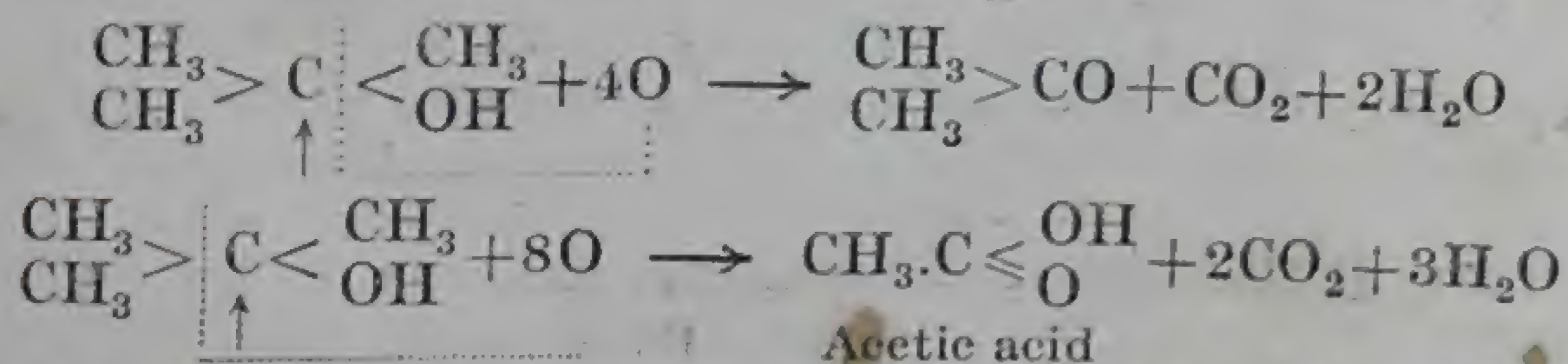
(ii) *Oxidation.* On oxidation, primary alcohols give at first aldehydes and then acids containing the *same* number of carbon atoms as the original alcohols ; *e.g.*,



Secondary alcohols give ketones containing the *same* number of carbon atoms :—

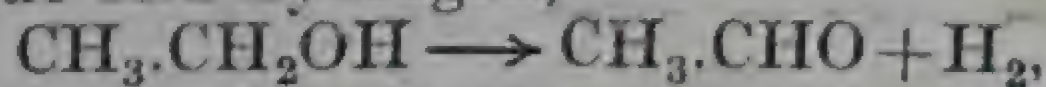


Tertiary alcohols, since they contain no hydrogen directly linked to the hydroxyl-bearing carbon atom, do not readily undergo oxidation. On prolonged treatment with strong oxidizing agents, their molecules *break up*, yielding ketones and carboxylic acids, each containing a *smaller* number of carbon atoms than the alcohol itself. Thus trimethyl carbinol $(\text{CH}_3)_3\text{C.OH}$, yields, on vigorous oxidation, acetone, acetic acid, and carbonic acid :—



In these reactions, an oxygen atom enters the molecule of a tertiary alcohol, attaching itself to the carbon atom carrying the hydroxyl group and driving out from the molecule either (a) one alkyl and one hydroxyl group, or (b) two alkyl groups.

(iii) *Action of Hot, Reduced Copper.* When the vapour of an alcohol is passed over reduced copper heated at 300° , different products are obtained according to the nature of the alcohol. If it be primary, it yields an aldehyde and hydrogen,



if secondary, a ketone and hydrogen,



and if tertiary, an olefine and water,



115. Distinction between Primary, Secondary and Tertiary Alcohols :—

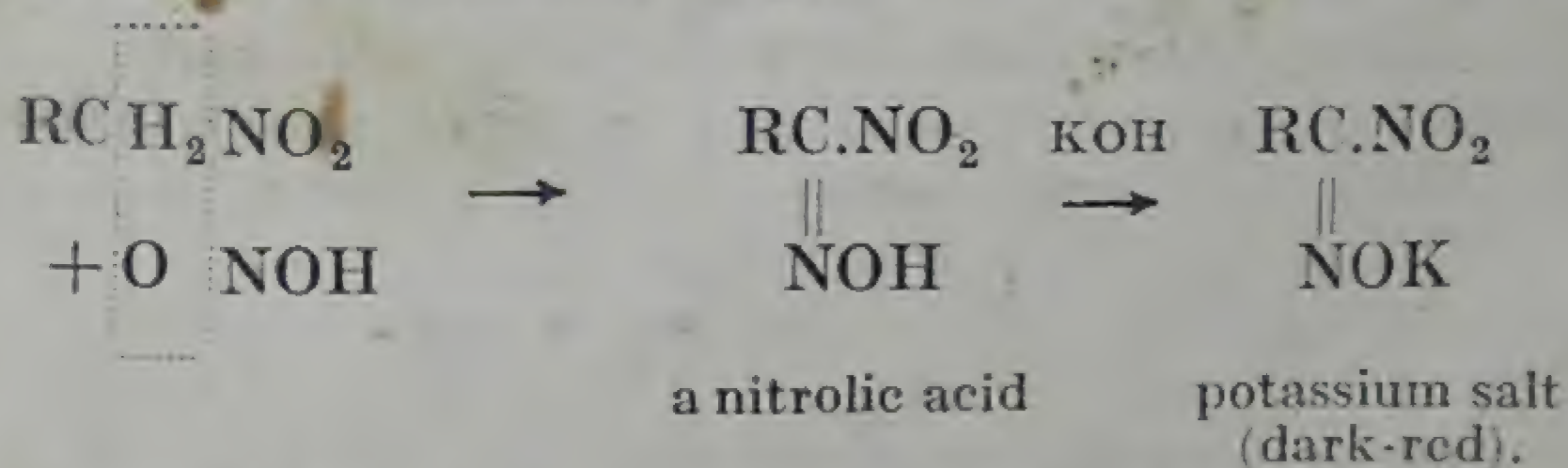
(1) *Behaviour on Oxidation.* See Sec. 114.

(2) *Action of Hot Reduced Copper.* See above.

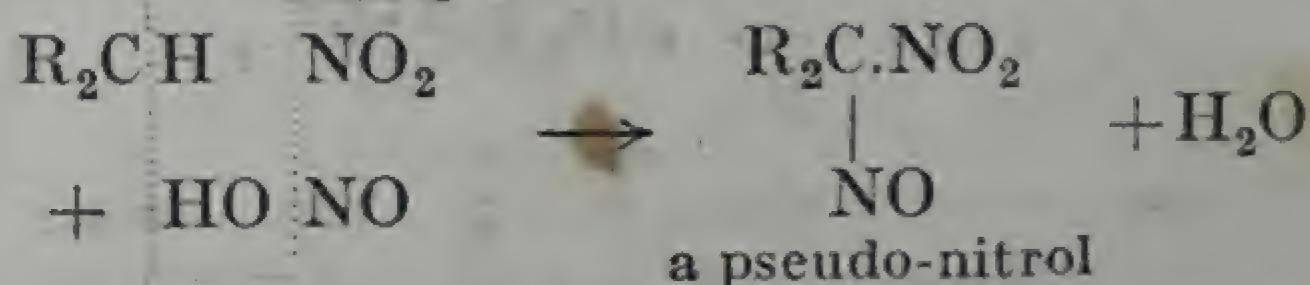
(3) **Victor Meyer's Method.** An indirect method of distinguishing between a primary, a secondary and a tertiary alcohol is first to convert it into the corresponding *nitroparaffin* by successive treatment with HI and AgNO_2 . The nitroparaffin is then dissolved in KOH solution, sodium nitrite is added, the solution is acidified with dilute sulphuric acid, and then again made alkaline. The production of a blood-red coloration shows it to be a primary, a blue coloration a secondary, and no coloration a tertiary alcohol.

The distinction is based on the different behaviour of the corresponding nitroparaffins towards nitrous acid :

The primary nitroparaffins react with nitrous acid, yielding nitrolic acids, which dissolve in alkalies to give dark-red solutions :

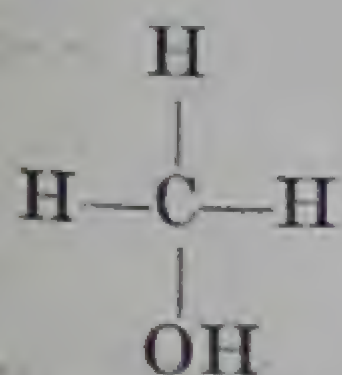
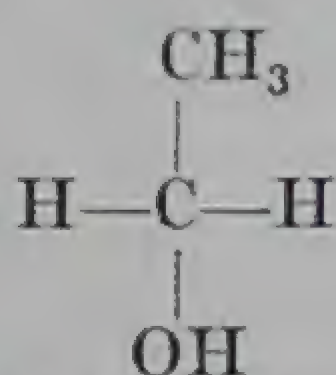
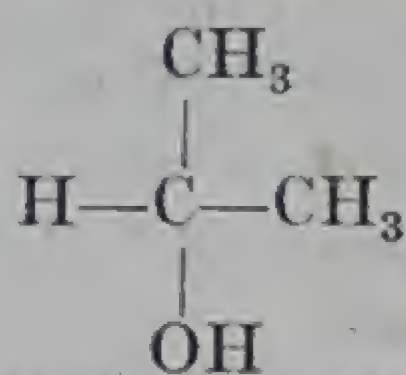
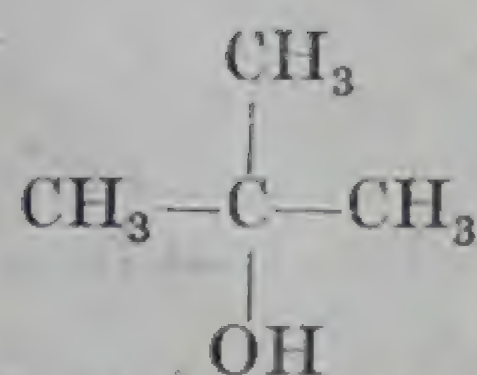


The secondary nitroparaffins react with nitrous acid, yielding blue-coloured nitro-nitroso compounds called, pseudonitrols :



The tertiary nitroparaffins, since they contain no hydrogen directly linked to the carbon carrying the nitro group, do *not* react with nitrous acid.

(4) *The Steric Influence of the Alkyl Groups on the Reactivity of the Hydroxyl Group.* When 1 gram-molecule each of a primary, a secondary and a tertiary alcohol is separately heated with 1 gram-molecule of acetic acid under similar conditions, the rate at which esterification occurs and therefore the amount of the ester produced is the greatest in the case of the primary and the least in that of the tertiary alcohol. If we assume the rate of esterification of methyl alcohol to be 100, the rates for a few others are :—

Carbinol
100Methyl carbinol
45.7Dimethyl carbinol
5.4Trimethyl carbinol
1.4

The highest rate of esterification in the case of methyl alcohol is in accord with the fact that there is no alkyl group in union with the carbon atom carrying the hydroxyl group.

116. Methyl Alcohol, Methanol or Wood Spirit, CH_3OH .

Occurrence. Methyl alcohol occurs in the form of methyl esters in the essential oils of many plants, *e.g.* as methyl salicylate in oil of wintergreen (*Gaultheria procumbens*), as methyl benzoate in oil of cloves, and as methyl ester of anthranilic acid in oil of orange flowers.

Manufacture. Methyl alcohol is manufactured by two different methods:—

(1) *By Destructive Distillation of Wood.* The distillation of wood is usually carried out in large, horizontal retorts made of boiler plate (Fig. 64). The wood, after being cut into pieces of suitable size,

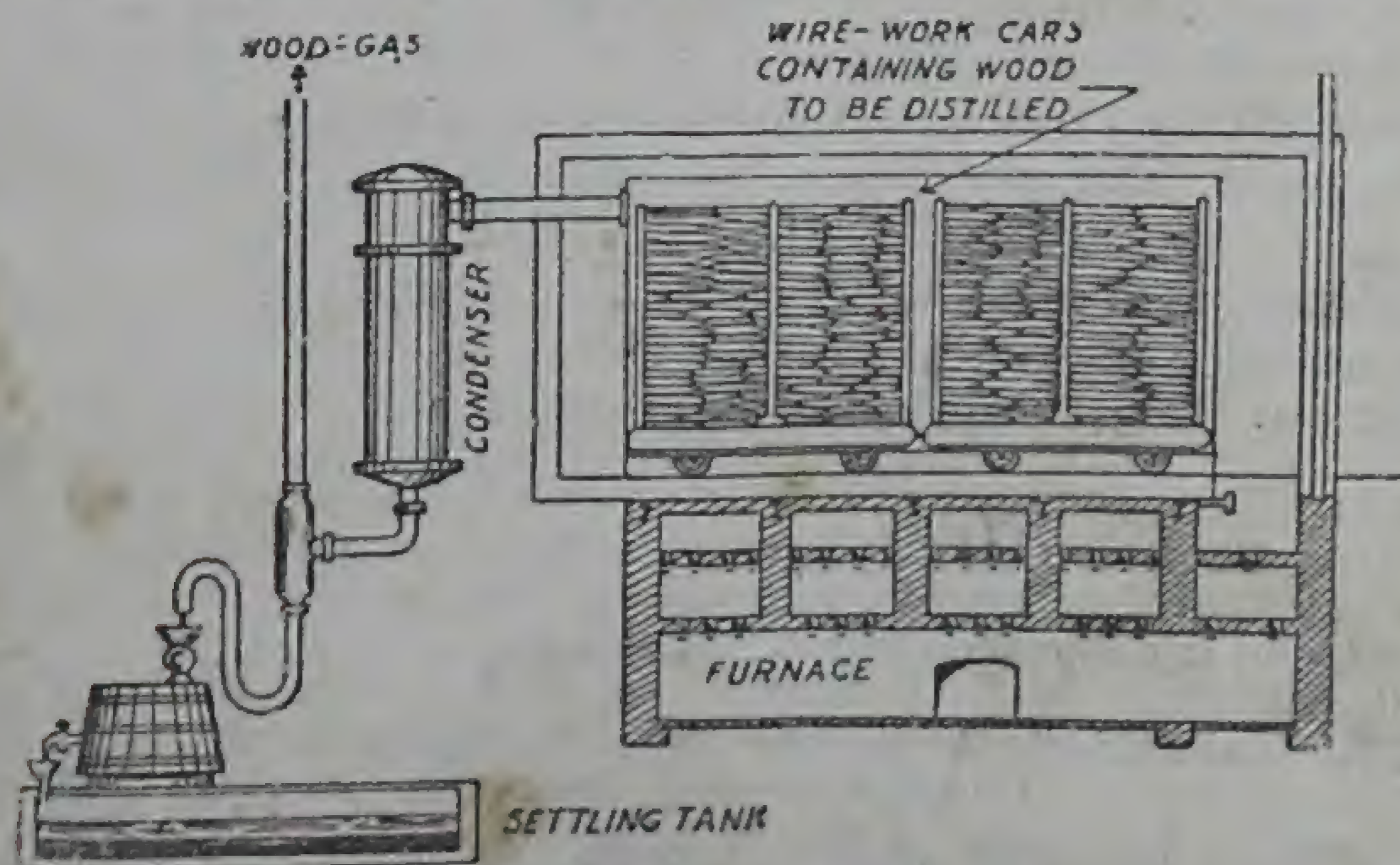


Fig. 64. Plant for the Distillation of Wood.

is put into wire-work cars mounted on wheels, which can be rolled in or out of the retorts as desired. The heating is effected by means of wood gas obtained during the process. As soon as the distillate begins to flow from the mouth of the condenser, the fire is turned low, as overheating causes a loss of volatile matter. Towards the end, the temperature is raised quite rapidly in order to drive out the heavy tars. The products of distillation are (i) wood gas, consisting mainly of CO , CH_4 and H_2 , (ii) an aqueous layer known as pyroligneous

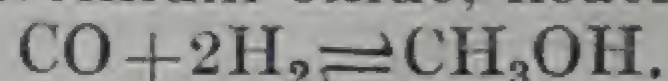
acid, which, in addition to a large proportion of water, contains acetic acid, acetone and methyl alcohol, and (iii) wood tar. The residue consists of charcoal, which is removed at the end of the operation when still hot, thus, saving the heat of the brick-work for the next charge.

The pyroligneous acid, which forms the upper layer, is run off from the wood tar, and distilled. The vapours are passed through hot milk of lime, which retains acetic acid as calcium acetate, while the methyl alcohol, acetone and water pass on.

The distillate, after being dehydrated with quicklime, is fractionated to obtain crude acetone (b.p. 56°) and crude methyl alcohol (b.p. 65°).

The crude methyl alcohol, obtained as above, is diluted with water in order to throw out of solution the oily impurities, which collect at the surface, and are run off. The aqueous layer, which still contains acetone and other impurities, is mixed with powdered anhydrous calcium chloride, whereby a crystalline compound of the composition $\text{CaCl}_2 \cdot 4\text{CH}_3\text{OH}$, separates out. This is gently heated to drive off acetone and is then decomposed by distillation with water. The distillate is finally dehydrated by repeated treatment with quicklime, and is then redistilled. The product thus obtained still contains traces of acetone and other impurities. (For further purification, see below).

(2) *From Water Gas (Patart Process).* Since 1923, large quantities of methyl alcohol are being produced synthetically. The process consists in passing a mixture of water gas ($\text{CO} + \text{H}_2$) and hydrogen, purified, from arsenic, sulphur and phosphorus compounds, under a high pressure (300 to 500 atmos), over a catalyst, consisting of a mixture of zinc oxide and chromium oxide, heated to about 400°C :—



The reaction gases are cooled to condense out the methyl alcohol, and the remainder recirculated over the catalyst.

Purification. Pure methyl alcohol is best obtained from the commercial product by heating it with anhydrous oxalic acid (prepared by heating oxalic acid crystals at 100°). On allowing the liquid to cool, di-methyl oxalate separates out as crystals. These are well drained on a filter-pump, washed with a little water, and then hydrolysed with caustic soda. The methyl alcohol, thus set free, is distilled off, and is dehydrated by distillation first over quick-lime and then over metallic calcium.

Expt. 39. To illustrate the process of the destructive distillation of wood. Fit

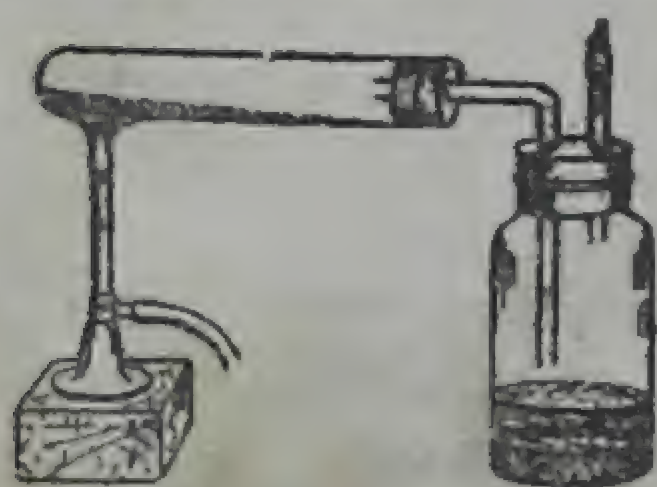


Fig. 65. Apparatus to illustrate the process of wood distillation.

up the apparatus shown in Fig. 65. Heat some saw dust in the test-tube. Notice that the distillate consists of (i) an upper layer of pyroligneous acid, and (ii) a lower layer of wood-tar. Show that the gas escaping at the upper end of the tube is combustible.

Properties. Pure methyl alcohol is a colourless liquid, which boils at 65° . It possesses an agreeable, wine-like odour and a burning taste, but is poisonous. Many cases of blindness or death have been caused by drinking mixture containing methyl alcohol. Blindness may

also result from prolonged exposure to its vapour. It burns with a plane, non-luminous flame, and its vapour forms an explosive mixture with air. It is miscible with water in all proportions.

Methyl alcohol possesses the general chemical characters of an alcohol (Sec. 114).

Constitution. See Sec. 40.

Detection. The presence of methyl alcohol can be readily detected by the formation of methyl salicylate or formaldehyde. It may be differentiated from ethyl alcohol by its failure to give the iodoform test.

Expt. 40. Identification of Methyl Alcohol. (i) Boil a few drops of methyl alcohol with a little salicylic acid and a drop or two of concentrated sulphuric acid. Notice the characteristic fragrant odour of methyl salicylate.

(ii) Place a few drops of methyl alcohol in a boiling-tube. Cover the same with some asbestos wool. Now heat a copper gauze to redness in an oxidizing flame and drop it immediately into the tube; notice the characteristic suffocating odour of formaldehyde.

(iii) Repeat Expt. 41, (Sec. 120), using pure methyl alcohol instead of ethyl alcohol. No iodoform can be detected.

Uses. (1) The largest use for methyl alcohol is as a denaturant for ethyl alcohol.

(2) About an equal quantity is oxidized to formaldehyde, which is used in the production of Bakelite.

(3) Large quantities of methyl alcohol are used in the manufacture of dimethylaniline, dyes, drugs and perfumes.

117. Ethyl Alcohol, *Ethanol*, $\text{CH}_3\text{CH}_2\text{OH}$.

Occurrence. Ethyl alcohol occurs naturally in the form of its esters with organic acids in many essential oils and fruits.

Manufacture. Ethyl alcohol is manufactured on a large scale from three different sources:

(1) Saccharine materials, *e.g.*, molasses from the manufacture of cane-sugar.

(2) Starchy substances, such as potatoes, barley, corn and rice.

(3) Ethylene obtained (among other gases) by "cracking" petroleum or natural gas¹.

The production of pure alcohol or *rectified spirit* from the first two sources consist of three main steps: (1) *Fermentation* (2) *Distillation*, and (3) *Rectification*.

(1) **Fermentation.** The sugar can be directly subjected to alcoholic fermentation, while starch must first be converted into a sugar called *maltose*.

¹ The process is based on the addition of the elements of water (Sec. 85), but no details are at present available.

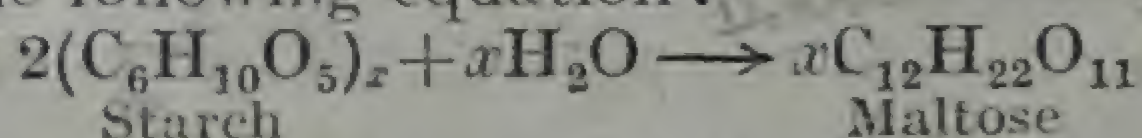
(a) **Production of Alcohol from Sugar.** In the case of saccharine materials, fermentation is directly effected by means of yeast (*Saccharomyces*. Sec. 66). The sugar is generally employed in the form of "molasses"—a dark-coloured, syrupy liquid obtained in the manufacture of cane sugar, from which the sugar cannot be profitably extracted. This contains about 55 per cent by weight of sugar, together with inorganic salts. It is diluted with water to a sugar concentration of 10 to 12 per cent and acidified with sulphuric acid to prevent infection by undesirable organisms. The liquid is heated to about 30°C, and yeast is added to start the fermentation which is complete in about 13 hours, when yeast is filtered off, and the fermented liquor, technically known as the "wash", is subjected to distillation.

The reactions taking place during the fermentation of sugar have already been explained (Sec. 66.)

(b) **Production of Alcohol from Starch.** The production of alcohol from starch consists of two distinct steps: (i) conversion of starch into maltose (*saccharification*) and (ii) alcoholic fermentation.

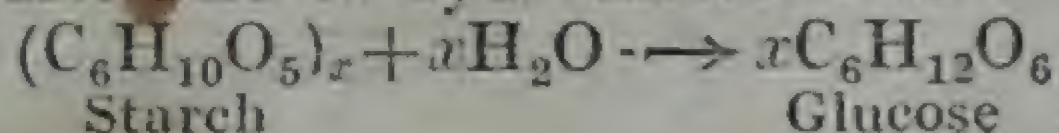
(i) **Saccharification.** The conversion of starch into maltose is brought about by means of an enzyme, called diastase, which is produced during the germination of corn, and is also found in saliva and the pancreatic juice. The diastase is not used as such, but is employed together with the whole corn in the form of malt, which is most conveniently obtained by the germination of barley. Barley is malted by allowing it to germinate in the dark at 15°, in layers about 5 inch thick. The germination is then stopped by raising the temperature, and the malt is crushed and extracted with water. The resulting liquid, known as the malt-extract, contains diastase in solution.

Potatoes, rice, maize, or unmalted barley are employed as the usual source of starch. They are rasped or crushed and then gelatinized by treatment with super-heated steam. The resulting mass is mixed with water, and some ground malt, or malt extract, is added. The temperature is maintained at 60° to 62°C, until the conversion of starch into maltose is practically complete (about 20 minutes). The liquid is then boiled in order to stop the action of diastase. The conversion of starch into maltose, which is a hydrolytic action, is represented by the following equation:

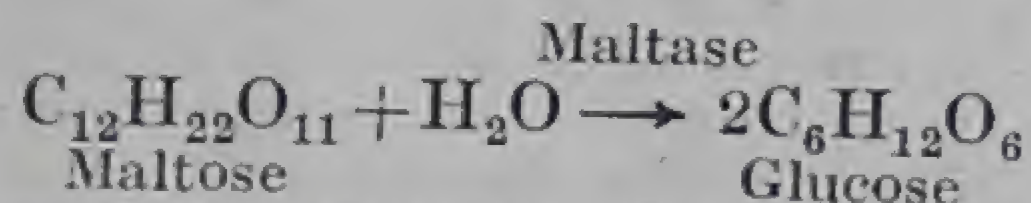


The process is known as mashing and the product as *mash* or *wort*.

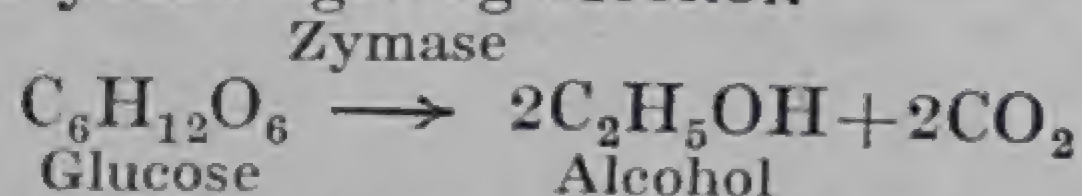
As an alternative, starch is converted into sugar (glucose) by means of hot dilute sulphuric acid or hydrochloric acid:



(ii) *Alcoholic Fermentation.* The saccharine liquid obtained by either of the processes described in (i) is fermented by means of *yeast* at a temperature not exceeding 33°C . The fermentation takes three to four days for completion. In the case of "mash", the maltose present is first decomposed into glucose by the enzyme, maltase, contained in the yeast:



The glucose formed is at once decomposed by *zymase*—another enzyme present in yeast—giving alcohol.



During fermentation, frothing of the liquid occurs, owing to the evolution of carbon dioxide.

In case the starch has been saccharified by means of dilute sulphuric acid or hydrochloric acid, the glucose present is directly attacked by *zymase*, producing alcohol.

(2) *Distillation.* The fermented liquid, which contains not more than 18 per cent of alcohol, is subjected to fractional distillation. This, in modern plants, is effected in one step and continuously.

In Great Britain, the fractionation is carried out in the Coffey still (Fig. 66),

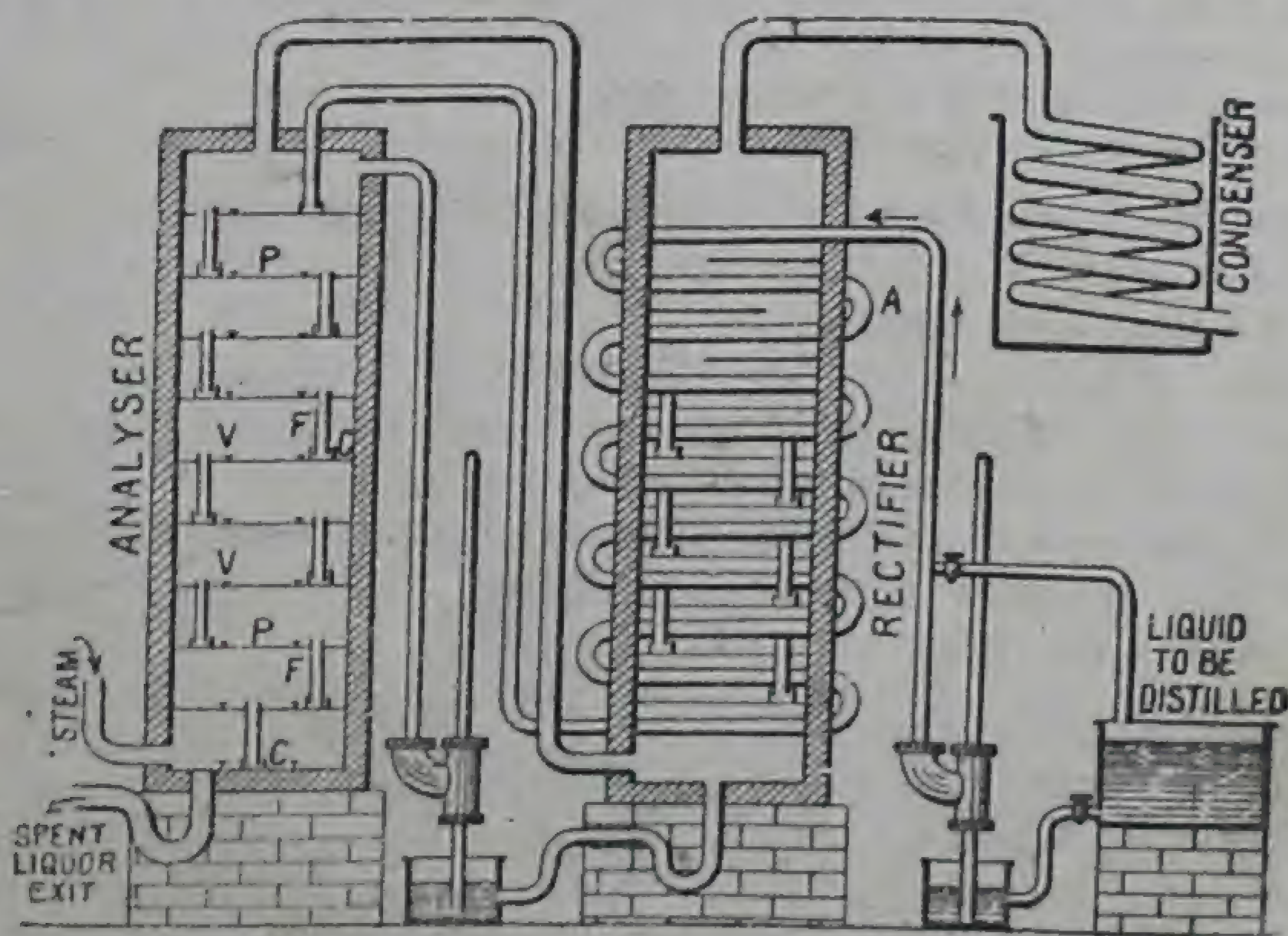


Fig. 66. Coffey Still.

which was patented by Aeneas Coffey in 1832. It consists essentially of a combination in series of two fractionating columns, known as the *analyser* and the *rectifier*. The "analyser" (shown on the left) is divided into a series of chambers

by horizontal plates, *P*, perforated with holes and furnished with valves, *V*, opening upwards. From each of these, an overflow pipe, *F*, passes down and dips into a shallow cup, *C*, on the next lower plate. The cup holds a sufficient amount of liquid to form a hydraulic seal at the lower end of each overflow pipe. The overflow pipes project about 1 inch or so above the perforated plates, thus determining the depth of the liquid layer on each plate. The lower half of the "rectifier" is also divided into chambers by perforated plates, and is provided with overflow pipes. Through the chambers of the rectifier pass coils of pipe, *A*, through which the liquid to be distilled flows on its way to the analyser.

The Coffey still works on the counter current principle. The liquid to be distilled passes downwards through the coils of pipe in the rectifier, where it gets heated (by steam and alcohol vapour) nearly to its boiling point and is then discharged at the top of the analyser. Free steam from a boiler is admitted at the base of the analyser, and, passing upwards through the thin layers of liquid on the perforated plates, carries with it the vapour of alcohol and other volatile substances present in the fermented liquid. In each one of the chambers, there occurs an exchange of constituents between the liquid layer and the vapours; the alcohol present in the liquid evaporates while the water vapour from the gaseous phase undergoes condensation (compare page 17). This process is repeated in each chamber and the ascending mixture of vapours, therefore, gets continuously richer in alcohol while downcoming liquid gets progressively poorer in alcohol.

The vapour of alcohol, etc. passes out of the analyser at the top, and then enters the rectifier at its base. During its upward passage, practically the whole of the water vapour gets condensed by an action similar to that taking place in the analyser, and also by coming into contact with coils of pipe conveying the cold fermented liquid. Hence only the alcohol vapour passes out at the top of the rectifier, and is conveyed to the condenser. The water condensed in the rectifier contains some alcohol, and is, therefore, conveyed to the top of the analyser, where it mixes with the fermented liquid. The spent liquor, entirely deprived of its volatile constituents, is drawn off at the base of the analyser.

The raw spirit obtained by distillation contains from 90 to 95.57 per cent of alcohol. The latter limit represents the constant boiling mixture of alcohol and water, and boils at 78.13° . For industrial purposes, such as when used as a fuel or in making varnishes etc., the raw spirit is *denatured*, *i.e.*, rendered unfit for drinking by the addition of about 10 per cent of wood spirit or methyl alcohol, and a small quantity of paraffin oil, or by the addition of crude rubber distillate. The product, known as methylated spirit or denatured alcohol, is sold duty-free.

Rectification. When required for internal use, *e.g.*, for the preparation of spirits, liquors, pharmaceutical tinctures, etc., the raw spirit must be freed as much as possible from oily mixture of higher alcohols, known as fusel oil, which the raw spirit always contains, as well as from low-boiling impurities, such as acetaldehyde. Formerly, fusel oil was removed from the crude spirit by dilution with water and filtration through charcoal, but at the present time fractional distillation is relied upon. The crude spirit is submitted to

very careful fractional distillation in specially designed stills, and the following fractions are collected separately.

(i) *First runnings*, i.e., low boiling by-products, consisting chiefly of acetaldehyde.

(ii) *Rectified spirit*, consisting of pure ethyl alcohol (90—95.57%).

(iii) *Last runnings*, which consist of "fusel oil."

118. Absolute Alcohol. By this term is meant alcohol entirely free from water. As alcohol forms a constant-boiling mixture with water, it is not possible to effect a complete separation of the two liquids by fractional distillation. Other means must, therefore, be adopted. In the laboratory, the dehydration is effected by distillation over quicklime. The last traces of moisture (about 0.5 per cent) are then removed by treatment with a calculated amount of metallic sodium followed by redistillation.

Absolute alcohol, which, a few years back, was hardly known outside the laboratory, is now used as a solvent on a commercial scale. The removal of 4.5 per cent of water greatly increases the solvent power of alcohol for many substances. It mixes with gasoline and other hydrocarbons in all proportions, which the ordinary 95 per cent alcohol is incapable of doing. For commercial purposes alcohol is rendered anhydrous, by distilling a mixture of it with benzene.

In this process, advantage is taken of the fact that alcohol, water and benzene form a ternary mixture having a minimum boiling-point of 64.9° and containing :

Water,	7.4 per cent,
Alcohol,	18.5 " "
Benzene,	74.1 " "

Further, benzene and alcohol also form a minimum boiling mixture, which boils at 68.2° and consists of

Alcohol,	32.4 per cent.
Benzene,	67.6 " "

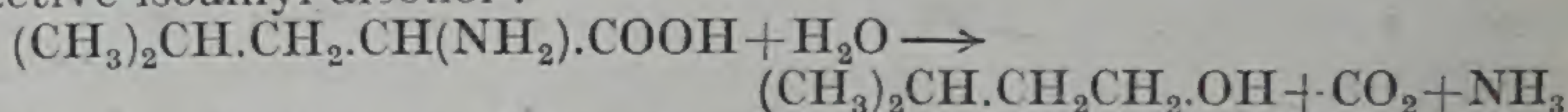
On fractionally distilling aqueous alcohol containing a sufficient proportion of added benzene, the minimum boiling ternary mixture first passes over, until all the water has been eliminated. Then the binary mixture of alcohol and benzene passes over, until all benzene has been removed. The residual liquid in the still consists of absolute alcohol. The recovered benzene is utilized for the dehydration of a further quantity of alcohol.

119. By-Products of Alcohol Industry. The important by-products of the alcohol industry are :

(1) **Carbon dioxide.** During the fermentation, large quantities of carbon dioxide are removed. The gas is purified and compressed to the liquid state, and is sold either as such or in the solidified form for refrigeration purposes.

(2) **Head Products.** The more volatile constituents (chiefly acetaldehyde and volatile esters) present in the crude spirit pass over as "first runnings" or "head products" during the fractional distillation of crude spirit, and are collected separately.

(3) **Fusel Oil.** This is obtained as the “*last runnings*” or “*tail products*” during fractional distillation of crude spirit. It consists of an oily mixture of higher alcohols that are only moderately soluble in water. They are not produced from the sugar or starch as was formerly supposed, but by the disruption of certain amino-acids (particularly *leucine*, *isoleucine* and *valine*) present as such in the natural mash or produced from proteins of the raw material during the conversion of the mait into sugar. The decomposition is brought about by yeast to satisfy its need for nitrogen and for the production of enzymes, the higher alcohols being left behind as non-assimilable products of metabolism. Thus, *l*-leucine (α -aminoisobutyl acetic acid) gives inactive isoamyl alcohol :



Similarly, *l*-isoleucine gives rise to *l*-amyl alcohol, and *valine* to isobutyl alcohol.

The proportion of fusel oil in raw spirit is from 0.2 to 0.4 per cent. by volume. It may be increased by the addition of leucine and other amino-acids to the fermenting mash.

Fusel oil fetches a much higher price per gallon than the alcohol itself. It is chiefly used in the production of *commercial* amyl alcohol, (Sec. 124) which has numerous technical applications.

(4) **Spent Wash.** The “spent wash” *i.e.*, the liquid from which the alcohol has been recovered by distillation, contains all the proteins present in the starting material. It is utilized as a cattle food.

(5) **Argol or tartar.** This consists of crude potassium hydrogen tartrate, which, being insoluble in aqueous alcohol, separates during fermentation of grape-juice, as hard, brown crusts. It serves as the raw material for the manufacture of tartaric acid.

120. Properties of Ethyl Alcohol. Ethyl alcohol is a colourless mobile liquid, having a pleasant pungent odour. Absolute alcohol boils at 78.37° and has a sp.gr. of 0.789 at 20° .

Ethyl alcohol forms a constant-boiling mixture with water containing 95.6 per cent. of the alcohol and boiling at 78.13° . In dilute solutions, alcohol has a specific intoxicating effect on the system. The use of spirits and liqueurs is based on this property. Alcohol is an excellent solvent for many organic substances, such as resins and oils.

Alcohol burns with a pale blue non-luminous flame. It possesses the general chemical characters of an alcohol.

Nitric acid oxidizes ethyl alcohol with explosive violence, producing among other products, acetaldehyde, carbon dioxide and water.

Constitution. See under Sec. 40.

Detection. Ethyl alcohol can be readily detected as in the following experiments :

Expt. 41. Iodoform Test. Warm a small quantity of ethyl alcohol with crystal of iodine, and then add a solution of potassium hydroxide drop by drop until the iodine colour just disappears. A yellow precipitate of iodoform, possessing a characteristic odour, will separate out, either immediately, or after some time. This test is given by several other compounds including acetone.

Expt. 42. Ethyl Acetate Test. Warm some ethyl alcohol with glacial acetic acid and concentrated sulphuric acid. A pleasant fruity odour of ethyl acetate will be developed.

Estimation (Alcoholometry). The percentage of ethyl alcohol in a mixture of pure water and alcohol can be readily determined by noting the specific gravity of the mixture and then looking up the figure in a reference table. For instance, if the specific gravity is found to be 0.8605, at 15.5°, reference to the table would show that the sample contained 75 per cent of alcohol by weight. In the case of beers, wines, and spirits, the sugary and other extractive matters present influence the specific gravity to such an extent that a direct determination of specific gravity would be of no value. Hence, a measured quantity of the sample is submitted to distillation, until about one-half has passed over. The distillate, which contains practically the whole of the alcohol, is diluted with pure water to the original volume of the sample, and then the specific gravity of the solution is taken.

For revenue purposes, the standard is **Proof spirit** which in Great Britain contains 49.3 per cent by weight, or 57.1 per cent by volume, of alcohol. Spirits are termed *under* or *over* proof according as they are weaker or stronger than proof-spirit. Thus, 25° over proof means that 100 volumes of the sample contain as much of alcohol as 125 volumes of proof-spirit, whilst 25° under proof means that 100 volumes of the sample contains as much of alcohol as 75 volumes of proof-spirit.

121. Alcoholic Beverages. Alcoholic beverages may be divided into two classes : (1) distilled beverages, and (2) undistilled beverages. Beer and wine are the chief undistilled beverages.

Beer is made from barley and is flavoured by the addition of hops. It contains from 3 to 6 per cent of alcohol and small quantities of dextrin, sugar, dissolved carbon dioxide, and other substances.

Wine is made from the juice of ripe grapes by means of species of yeast which occur naturally in the bloom on the skin of the fruit itself. Natural wines contain from 8 to 15 per cent of alcohol and free sugar. Fermentation automatically stops with the attainment of 15 per cent alcohol content, owing to the inability of yeast to grow in solutions containing a higher proportion of alcohol.

In making champagne, the grape juice is allowed to ferment in tightly closed bottles. The carbon dioxide, therefore, remains

dissolved in the beverage, which consequently effervesces on the pressure being released.

Sweet fortified wines, such as port and sherry, contain about 20 per cent alcohol. They are made in the manner above indicated and the alcohol content is then made up by the addition of pure alcohol. Some flavouring agent and sugar are also added to impart relish.

Another undistilled alcoholic beverage is cider, which is made from apple juice by the action of yeast and other organisms occurring naturally on the fruit. It contains from 4 to 8 per cent of alcohol.

In making distilled spirits, the fermented liquid is subjected to distillation to increase the alcoholic content and to free the beverage from unpalatable constituents. They usually contain 40 to 50 per cent of alcohol.

Whisky is made from barley and gin from maize. The latter is flavoured with juniper. Brandy is made by distilling wine, and rum by the distillation of fermented molasses. Vodka is distilled from rye, and is the common form of strong drink used in Russia.

122. Uses of Ethyl Alcohol :—

(1) As already mentioned, ethyl alcohol is a constituent of *alcoholic beverages* used so extensively.

(2) In its various denatured forms, ethyl alcohol is the most extensively used organic solvent. It is used for this purpose in the laboratory, in making pharmaceutical tinctures, and in the preparation of varnishes and lacquers.

(3) It is also used as a *fuel* in spirit lamps and spirit stoves. The use of alcohol as a motor fuel has attracted much attention. It is not sufficiently volatile to give proper starting in cold weather. This difficulty is overcome by using a mixture containing about 25 per cent of ether or petrol. In Philippines, where alcohol is cheap and petrol dear, the usual composition for motor spirit is 75 per cent of ether. The mixture is denatured by adding small quantities (about 1 per cent each) of kerosene and aniline.

In Europe, each country for patriotic reasons has a 'national' motor fuel. The idea is to make the greatest possible use of domestic sources of alcohol and to reduce the importation of petrol. India should also give attention to this problem. While her resources of petroleum are very limited, she has practically unlimited potentialities for the production of alcohol. Full utilization must be made of the enormous quantities of molasses, that the ever-growing sugar industry is bound to produce, and also of wood shaving, waste straw, and the sulphite liquor from paper factories. All these materials can be made to yield alcohol by suitable fermentation processes.

(4) Large quantities of alcohol are used in the production of numerous organic compounds, such as ether, chloroform, dyes, alkaloids, perfumes and collodion.

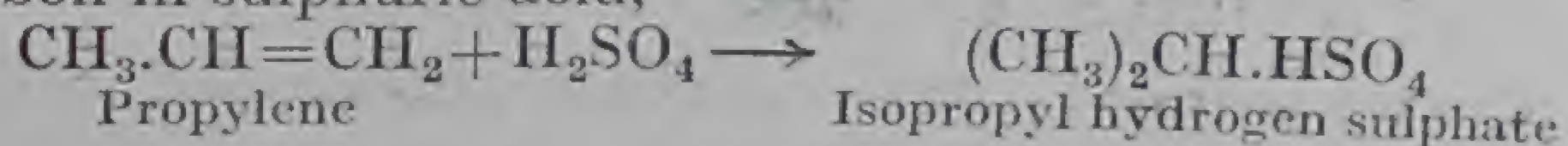
(5) Alcohol is also used as a *preservative* of biological specimens and as an *antiseptic* for the skin.

(6) Alcohol, in the form of brandy is much used by the allopathic physicians,

123. Propyl Alcohols, C_3H_7OH .

n-Propyl alcohol, 1-propanol, $CH_3.CH_2.CH_2OH$ (b.p. 97°), occurs in *fusel oil* (Sec. 119), from which it is obtained by fractionation. It has been extensively used in organic synthesis, but is of no commercial importance.

Isopropyl alcohol, 2-propanol, $CH_3.CH(OH).CH_3$ (b.p. 82°), is manufactured from propylene, obtained as a by-product in the cracking of heavy oils (Sec. 77). The process consists in absorbing the hydrocarbon in sulphuric acid,



and decomposing the resulting ester by the addition of water,



The gas from the cracking stills, containing about 15 per cent of the olefine hydrocarbons, is treated in towers with 87 per cent sulphuric acid, which absorbs propylene and butylene but not ethylene. The solution is run into warm water, and, after the separation of tarry matter, subjected to fractionation.

Isopropyl alcohol is nowadays used in industries under the name of *petrohol*¹. Large quantities are being used in the manufacture of isopropyl acetate which is employed as a solvent in lacquers. Petrohol is also used as a solvent in cosmetics and hair tonics, and in the manufacture of acetone.

124. Higher Alcohols.

n-Butyl alcohol, 1-butanol, $CH_3.(CH_2)_2.CH_2OH$ is obtained as a by-product in the manufacture of acetone by the fermentation of starch by means of *Bacillus macerans*. It is used—

(1) as a solvent, and

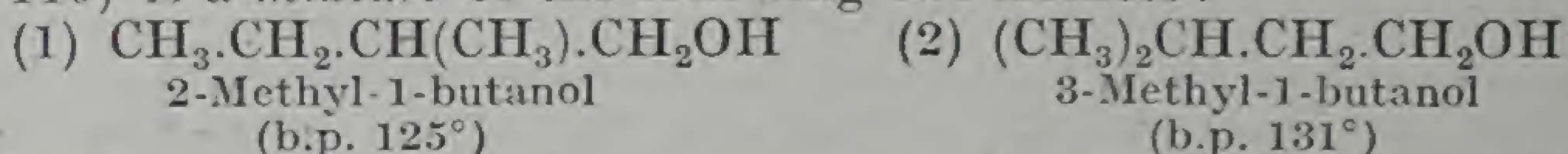
(2) in the manufacture of butyl acetate, $CH_3COOC_4H_9$, and dibutyl phthalate, $C_6H_4(COOC_4H_9)_2$, both of which are employed in lacquers.

Isobutyl alcohol, 2-methyl-propanol $(CH_3)_2CH.CH_2OH$, occurs in fusel oil, and has been extensively used in organic synthesis.

¹ The name suggests the origin (petroleum) and nature (alcohol) of the substance.

Tertiary butyl alcohol, or *trimethyl carbinol*, $(\text{CH}_3)_3\text{COH}$, is obtained from acetone with the aid of a Grignard reagent (page 169). It is one of the few lower alcohols that are solid at the ordinary temperature. It melts at 25°C and boils at 83°C .

Amyl alcohols, $\text{C}_5\text{H}_{11}\text{OH}$. All the eight isomeric amyl alcohols are known. Of these, four are primary, three secondary, and one tertiary. The commercial amyl alcohol, obtained from fusel oil (Sec. 119) is a *mixture* of the following two isomers:

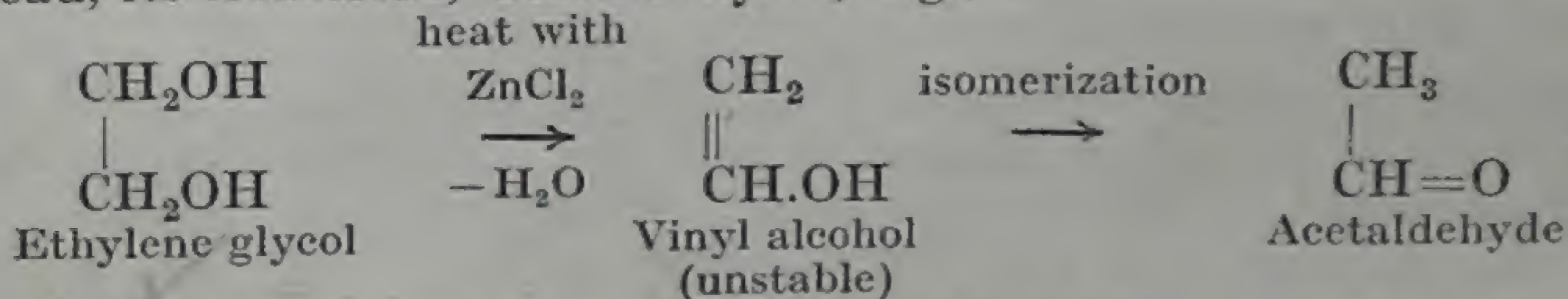


The former component is known as active¹ amyl alcohol and the latter as isoamyl alcohol. For commercial purposes, the mixture is used as such. Large quantities are converted into the corresponding mixture of amyl acetates, employed as a solvent in lacquers.

UNSATURATED ALCOHOLS

125. The unsaturated alcohols are derived from olefines or acetylenes, and consequently possess the dual character of an alcohol and an unsaturated compound. The olefine alcohols, $\text{C}_n\text{H}_{2n-1}\text{OH}$ or $\text{C}_n\text{H}_{2n}\text{O}$, are isomeric with aldehydes and ketones derived from paraffin hydrocarbons.

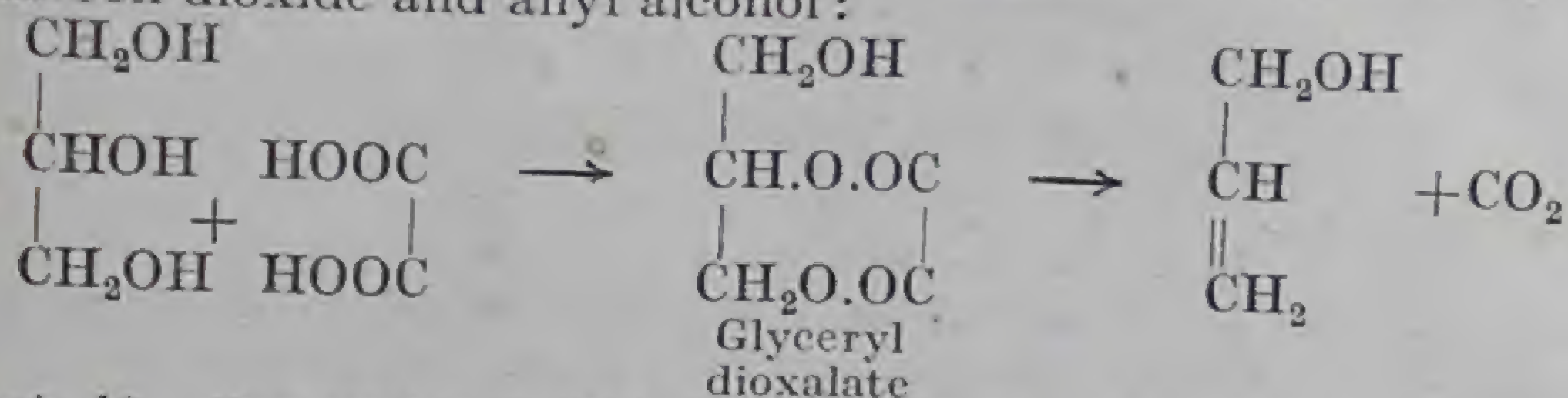
As in the case of unsaturated halogen derivatives (Sec. 102), two distinct classes of olefine alcohols are possible. However, the alcohols in which the OH group is directly united to a doubly bound carbon atom are unknown, since the grouping $>\text{C}=\text{CH}.\text{OH}$ is unstable and readily passes over into the group $>\text{CH}.\text{CH}=\text{O}$. An example of this class is vinyl alcohol, $\text{CH}_2=\text{CH}.\text{OH}$, traces of which are supposed to occur in commercial ether. It has never been isolated, since all reactions which might be expected to produce this substance yield, instead, its isomeride, acetaldehyde; *e.g.*,



126. Allyl Alcohol. *Vinyl Carbinol*, $\text{CH}_2=\text{CH}.\text{CH}_2\text{OH}$, 3-*Propenol*. This compound occurs in minute quantities in raw wood spirit. It may be obtained by the hydrolysis of allyl iodide by means of boiling water, but is usually prepared by heating glycerol with anhydrous oxalic acid to a temperature of 260°C . The reaction has been shown to occur in two stages, a glyceryl di-oxalate being formed

¹ as it is optically active (levorotatory)

as the intermediate product, which then gets decomposed by heat into carbon dioxide and allyl alcohol:

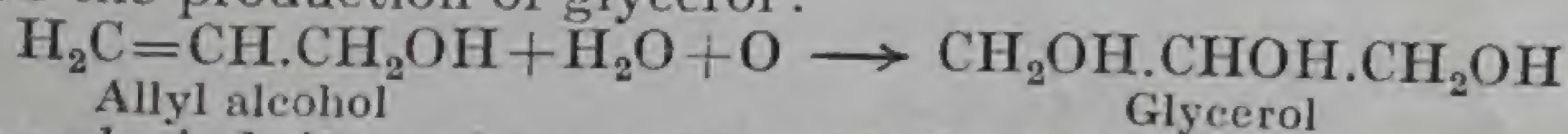


Expt. 42. Preparation of Allyl Alcohol. Distil a mixture of 30 gm. of oxalic acid and 100 c.c. of glycerol from a retort provided with a thermometer dipping into the liquid. Reject the distillate passing up to 180° , which contains formic acid. Then change the receiver, and collect the liquid passing over up to 260° , which contains allyl alcohol. Redistil this portion until the temperature reaches 105° . Dehydrate the distillate with anhydrous potassium carbonate, and then redistil.

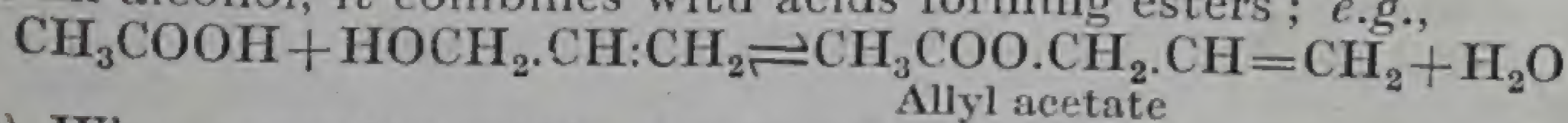
Notice (1), the odour of the liquid, and (2) its action on bromine water.

Properties. (1) Allyl alcohol is a colourless, pungent-smelling, mobile liquid boiling at 96.7° . It is miscible with water in all proportions.

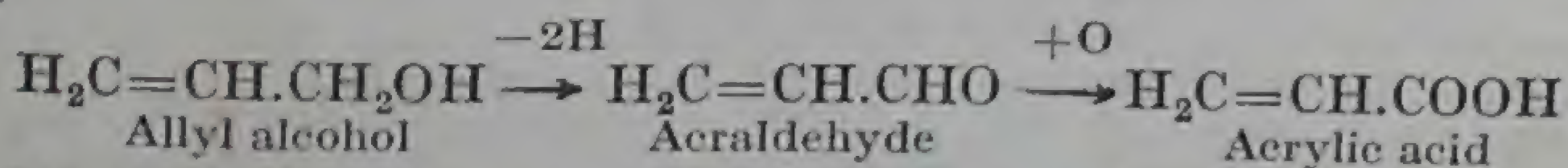
Allyl alcohol possesses two sets of properties, (i) those of an unsaturated compound, and (ii) those of a primary alcohol. As an unsaturated compound, it combines directly with hydrogen, halogens and halogen hydrides. When carefully oxidized with an alkaline solution of potassium permanganate, two hydroxyl groups are added on with the production of glycerol:



As an alcohol, it combines with acids forming esters; *e.g.*,

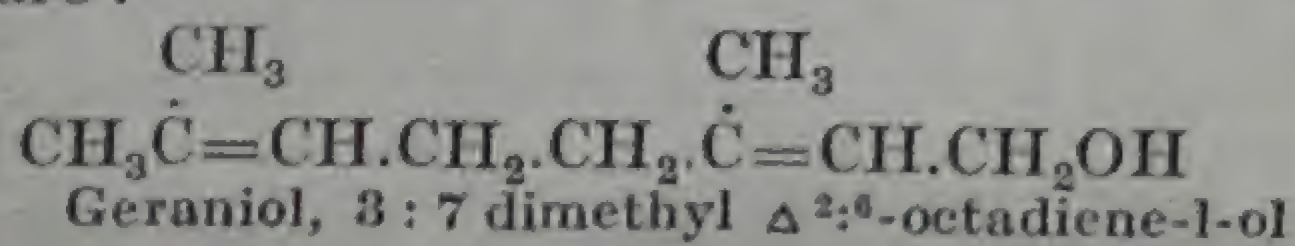


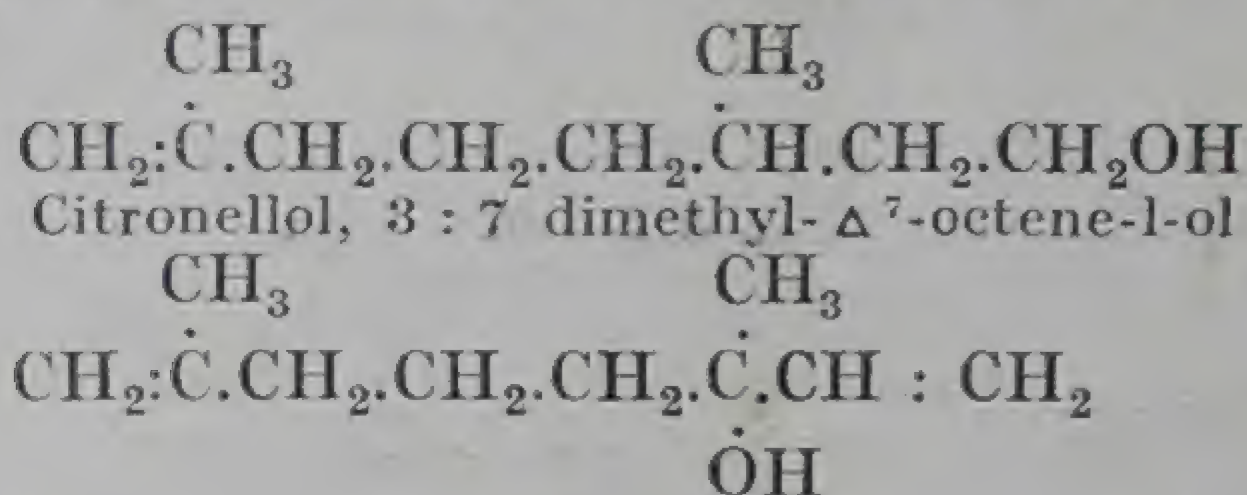
(2) When carefully oxidized with silver oxide, the primary alcohol group gets oxidized first to an aldehyde group and then to a carboxyl group:—



*126A. Olefinic or Open-Chain Terpene Alcohols.

Some of the higher unsaturated alcohols and their corresponding aldehydes occur in the essential oils of plants associated with *cyclic terpenes*, to which they are structurally related. These compounds are of great interest in perfumery. Three of the best known olefinic terpene alcohols are:





Linalol, 3 : 7-dimethyl- Δ 1:7-octadiene-3-ol

Geraniol occurs along with citronellol in otto of roses and in geranium oil. Rosha-grass oil contains about 90 per cent of free and combined geraniol.

Citronellol occurs in the *d*-form in citronella oil, and in the *l*-form in otto of roses.

Linalol occurs in oil of bergamot, lign-aloes and lavender.

* 126B. Propargyl Alcohol, *Propinyl Alcohol*, $\text{CH} : \text{C} . \text{CH}_2 \text{OH}$. This is the simplest of the acetylene alcohols. As a compound containing an acetylenic function it combines directly with four atoms of bromine, and forms explosive metallic derivatives with ammoniacal solutions of cuprous chloride and silver nitrate. It is a pleasant-smelling liquid boiling at 114° .

QUESTIONS

1. Write equations for reactions by which primary, secondary, and tertiary alcohols can be prepared. Describe one method, other than the oxidation method, by which the different types of alcohols can be distinguished.

(Punjab, B.Sc., 1933)

2. Starting with acetylene, outline a possible synthesis of (a) ethyl alcohol, (b) tertiary butyl alcohol.

(Punjab, B.Sc., 1932)

3. Explain the terms *primary*, *secondary* and *tertiary* as applied to alcohols. How would you distinguish between the three classes?

4. You are given an aliphatic alcohol. Describe how you would attempt to oxidize it, and then identify the product of oxidation. From your identification of the product of oxidation, what conclusions could you draw as to the constitution of the original alcohols?

(Punjab, B.Sc., 1929)

5. 0.2881 gm. of an alcohol, on being added to ethyl magnesium iodide, caused the evolution of 48.33 c.c. of ethane at 20° and 755 mm. Calculate the molecular weight of the alcohol.

(Ans. 144)

6. The analysis of an organic substance gave the following results; 0.2115 gm. on combustion gave 0.4655 gm. CO_2 and 0.2533 gm. H_2O . The vapour density of the substance was 29.7. When treated with potassium dichromate and dilute sulphuric acid, it produced a substance which gave the iodoform test. What was the original compound?

[Ans. Isopropyl alcohol, $(\text{CH}_3)_2\text{CH} . \text{OH}$].

7. Describe a method for the manufacture of methyl alcohol. What impurities would you expect in the alcohol manufactured by the process you are describing?

(Punjab, Inter., 1932)

8. What are the main products obtained by the dry distillation of wood? How are these products separated and purified? State to what commercial uses they are applied.

(Punjab, B.Sc., 1924)

9. How would you test for methyl alcohol in the presence of ethyl alcohol?

(Punjab, B.Sc., 1933)

10. Give an outline of the process of manufacture of industrial alcohol?

(Punjab, B.Sc., 1936)

11. Give an account of the various processes concerned in the preparation of ethyl alcohol from starch.

(Punjab, B.Sc., 1933)

12. Describe the preparation and important properties of allyl alcohol.

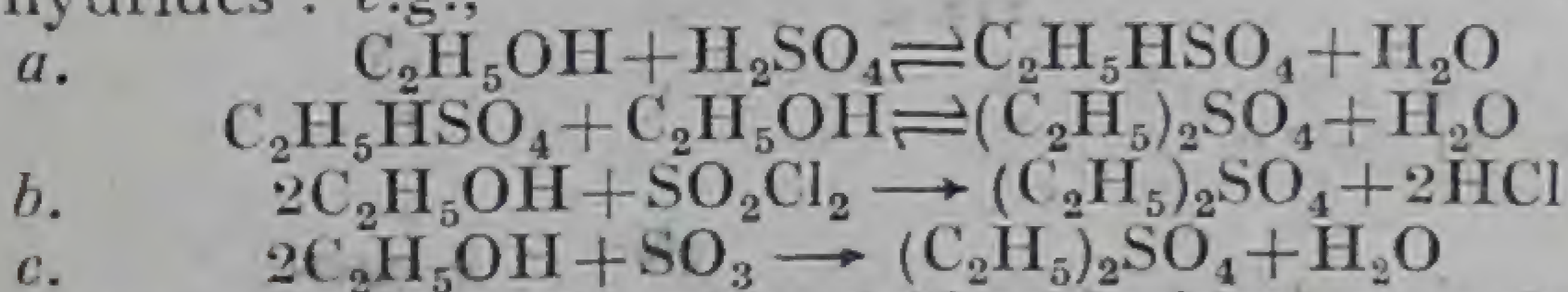
CHAPTER XV

ESTERS OF MONOHYDRIC ALCOHOLS WITH INORGANIC OXY-ACIDS

General. Esters or *ethereal salts*, as they are sometimes incorrectly called, are salt-like compounds each of which is formed by the interaction of an alcohol with an inorganic acid. The esters of halogen hydracids, or *alkyl halides*, have already been described (Chapter XII). In this Chapter the esters of inorganic oxy-acids will be taken up.

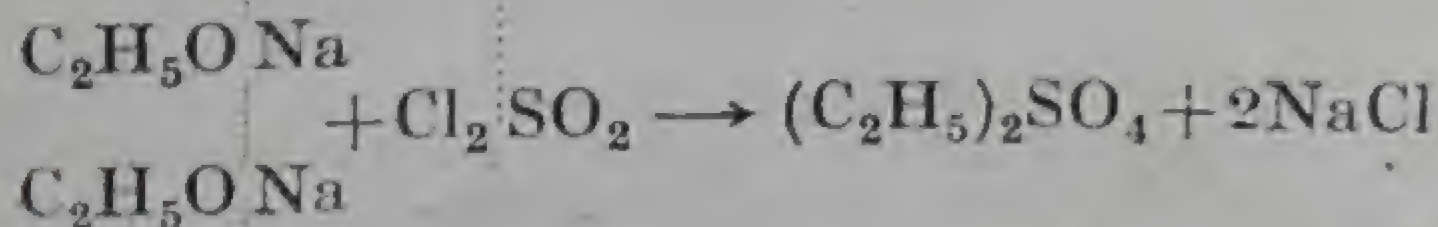
127. General Methods of Formation:—

(1) *From alcohols.* The esters of inorganic oxyacids may be obtained from the alcohols by the action of acids, acid chlorides, or acid anhydrides : *e.g.*,



The reaction of alcohols with acid chlorides or anhydrides is of special importance for the preparation of *normal* esters of polybasic acids.

(2) *From Sodium Alkoxides.* A better method of preparing normal esters of polybasic acids consists in treating sodio-derivatives of alcohols with acid chlorides ; *e.g.*,



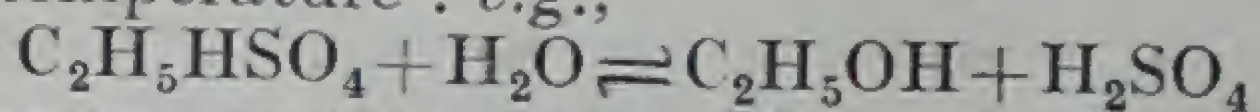
(3) *From Alkyl Halides.* When an alkyl halide is distilled with the silver salt of an oxy-acid, there occurs a double decomposition between the two, and the ester of the oxy-acid passes over ; *e.g.*,



128. Reactions. The most important reaction of the esters of inorganic oxyacids is their hydrolysis by aqueous alkalies, when the component alcohol is set free ; *e.g.*,



Acid esters are often hydrolysed merely on being mixed with water at the ordinary temperature : *e.g.*,

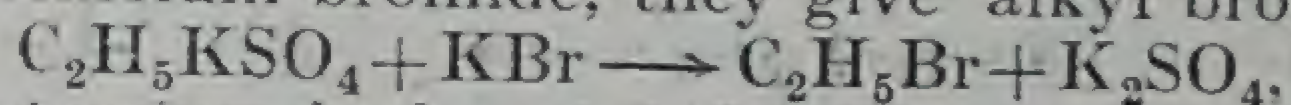


The action however, occurs more readily on boiling.

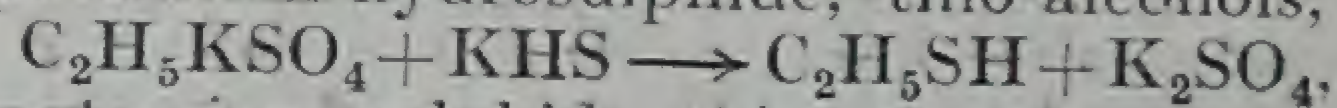
129. Alkyl Hydrogen Sulphates. Alkyl hydrogen sulphates, *i.e.*, acid esters of sulphuric acid, are obtained either (1) from alcohols by the action of concentrated sulphuric acid, or (2) from the olefine hydrocarbons, by treatment with sulphuric acid of proper concentration.

Alkyl hydrogen sulphates are acidic in reaction, and their metallic salts are mostly soluble in water. The potassium alkyl sulphates crystallize well, and, like alkyl halides (Sec. 97) are used as synthesizing agents. When heated or subjected to dry distillation with suitable reagents, they yield certain classes of organic compounds. Thus,

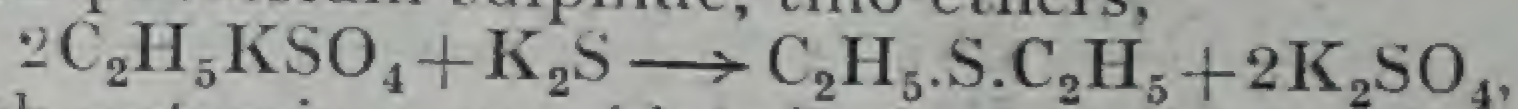
(1) with potassium bromide, they give alkyl bromides,



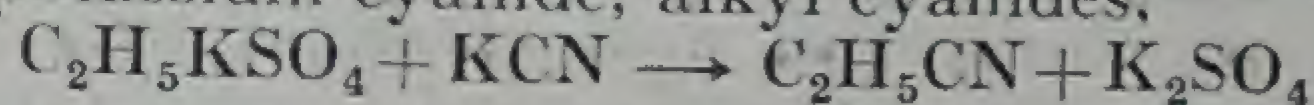
(2) with potassium hydrosulphide, thio-alcohols,



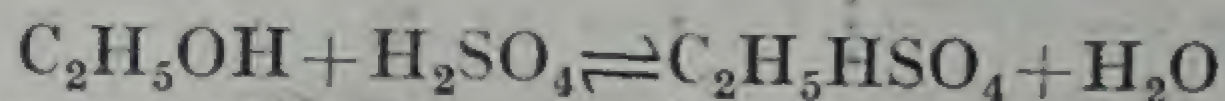
(3) with potassium sulphide, thio-ethers,



and (4) with potassium cyanide, alkyl cyanides,

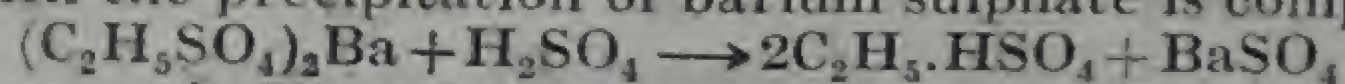


130. Ethyl Hydrogen Sulphate, Ethyl Sulphuric Acid, $\text{C}_2\text{H}_5\text{HSO}_4$. This is the most important representative of its class, and is obtained by the interaction of ethyl alcohol and concentrated sulphuric acid.



The yield is never quantitative, as the reaction attains an equilibrium.

Expt. 44. Preparation of Ethyl Hydrogen Sulphate. A mixture of equal volumes of alcohol and concentrated sulphuric acid is heated for about one hour on a steam bath under a reflux condenser. The reaction mixture is cooled, diluted with water, and treated with barium carbonate to neutralize the unchanged sulphuric acid and to convert ethyl hydrogen sulphate into barium ethyl sulphate. The barium sulphate and the excess of barium carbonate are filtered off, and the solution of barium ethyl sulphate is treated with cold dilute sulphuric acid, until the precipitation of barium sulphate is complete : -



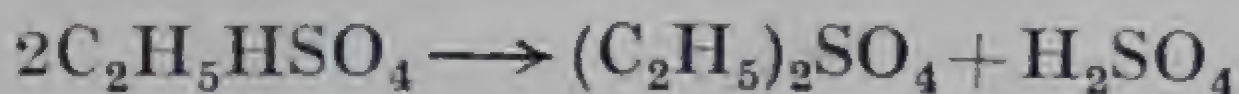
The solution is once again filtered, to remove barium sulphate, and then evaporated at the room temperature, under reduced pressure. Water and alcohol pass off, while ethyl hydrogen sulphate remains behind as a thick sour liquid.

Ethyl hydrogen sulphate is an odourless oily liquid. It has a strongly acidic reaction, and is miscible with water in all proportions. The more important reactions of ethyl hydrogen sulphate are :

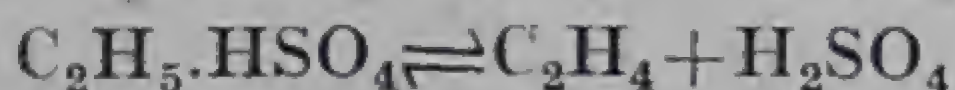
(1) The aqueous solution of the ester undergoes hydrolysis, yielding free sulphuric acid and ethyl alcohol, the reaction being slow at the ordinary temperature.

(2) It forms readily soluble metallic salts, the potassium salt being used in the synthesis of certain ethyl compounds (Sec. 129).

(3) When heated alone, it yields free sulphuric acid and diethyl sulphate :



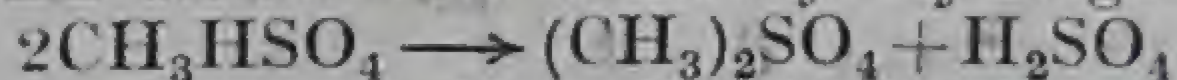
At the same time, free sulphuric acid and ethylene are produced (Sec. 87) :



(4) When it is heated with alcohol, diethyl ether, $\text{C}_2\text{H}_5.\text{O}.\text{C}_2\text{H}_5$, is obtained :



131. Dimethyl Sulphate, $(\text{CH}_3)_2\text{SO}_4$. This is the most important normal ester of sulphuric acid. It is obtained on a large scale by the vacuum distillation of methyl hydrogen sulphate¹ :

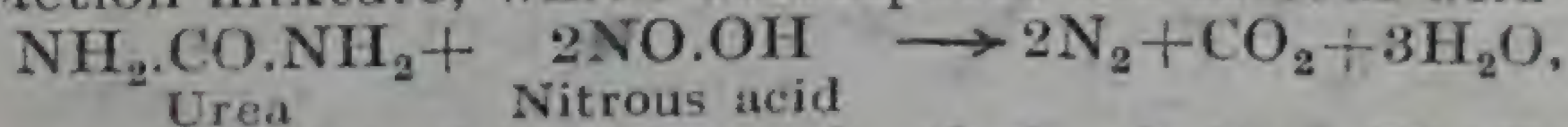


Dimethyl sulphate is a colourless liquid, boiling at 188° . It strongly attacks the mucous membranes and is very poisonous.

Dimethyl sulphate is a valuable methylating agent and is employed as such in the laboratory and on a commercial scale. It may be used with advantage in all reactions where methyl iodide is employed, though ordinarily only one of the two methyl groups is utilized. It reacts more readily than methyl iodide, and gives better yields. It is of particular importance in the methylation of primary and secondary amines and etherification of phenols.

132. Ethyl Nitrate, $\text{C}_2\text{H}_5\text{NO}_3$. When ethyl alcohol is treated with concentrated nitric acid, the oxidation of the alcohol occurs far more rapidly than esterification. Further, the oxides of nitrogen produced in the reaction attack the alcohol, yielding ethyl nitrite. The reaction is highly exothermic, and, unless proper care is taken, may become almost explosive in violence.

To overcome the above difficulty, a little urea is added to the well-cooled reaction mixture, which decomposes the nitrous acid formed,



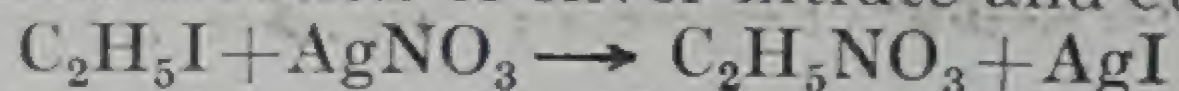
and thus prevents the formation of ethyl nitrite. Further, in the

¹ Methyl hydrogen sulphate is commercially obtained by the interaction of methyl alcohol and fuming sulphuric acid.

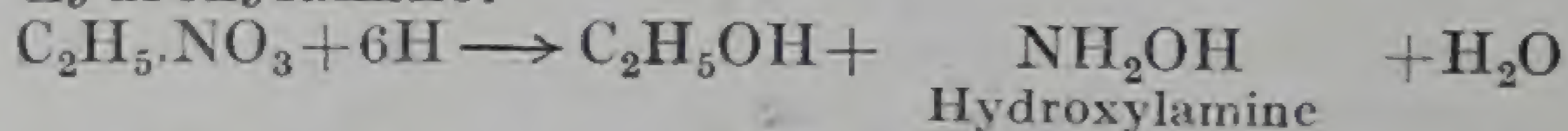
presence of urea, the reaction takes place quietly, and ethyl nitrate is the principal product.

Expt. 45. Preparation of Ethyl Nitrate. Place 15 c.c. of nitric acid (sp. gr. 1.4) and about 5 grams of urea in a large-sized round bottom flask. Cool the flask with ice, and add gradually to the mixture 30 c.c. of ethyl alcohol. When all the alcohol has been added, attach a Liebig condenser to the flask, and heat it *very slowly* on a water-bath. Wash the distillate (consisting of the ester and unused alcohol and acid) with water in a separating funnel. Dry the ester layer with fused calcium chloride, and redistil the dry ester from a water-bath.

Ethyl nitrate may also be obtained by the double decomposition between an alcoholic solution of silver nitrate and ethyl iodide.



Ethyl nitrate is a colourless liquid (sp. gr. 1.1) boiling at 87°. It has a pleasant odour, is practically insoluble in water but readily soluble in alcohol or ether. It burns with a luminous flame, and if thrown on a hot surface, may explode. It is hydrolysed by boiling water and hot alkalies. On reduction with tin and hydrochloric acid, it gives hydroxylamine.



133. Ethyl Nitrite, $\text{C}_2\text{H}_5\text{NO}_2$. This is the ethyl ester of nitrous acid, and has the structure $\text{C}_2\text{H}_5\text{O}-\text{N}=\text{O}$.

Preparation. Ethyl nitrite is prepared by the interaction of ethyl alcohol and nitrous acid. The latter, being unstable, is formed *in situ* by the action of dilute sulphuric acid on sodium nitrite.

A well-cooled mixture of equal quantities of ethyl alcohol and concentrated sulphuric acid is slowly added to a well-cooled solution of sodium nitrite in water. Brisk reaction sets in with the evolution of brown fumes of nitrogen tetroxide. After the action is over the ester (which rises to the top as an oil) is separated, washed, dried over calcium chloride, and distilled.

Properties. Ethyl nitrite is a colourless, insoluble liquid with a pleasant apple-like odour. It boils at 17°. When treated with boiling water, or dilute alkali, the ester is readily hydrolysed:



Distinction from Nitro-ethane. Ethyl nitrite and other alkyl nitrites differ from isomeric nitroparaffins in structure and properties (refer to nitro-ethane under nitro-paraffins).

Use. In the form of sweet spirit of nitre (which is an alcoholic solution of the ester) ethyl nitrite is used in medicine in mild febrile attacks.

134. Amyl Nitrite, $\text{C}_5\text{H}_{11}\text{NO}_2$. This substance is obtained by leading nitrogen trioxide into commercial amyl alcohol. It is a

yellow liquid consisting chiefly of *isoamyl nitrite*. It is used in medicine for relieving cardiac pain, and also in the preparation of nitroso- and diazo-compounds.

QUESTIONS

Jaliamwale
Bagh

1. Give the general methods for the preparation of esters of inorganic oxyacids.
2. Describe the preparation of ethyl sulphuric acid, and give its important reactions. To what use is its potassium salt put in synthetic organic chemistry?
3. Given sulphuric acid, and alcohol, what compounds can be prepared? Give practical details. (Punjab, Inter., 1919)
4. How is dimethyl sulphate prepared? To what use is it put in organic synthesis?
5. Describe the preparation of a pure sample of ethyl nitrate in the laboratory. What happens when ester is subjected to reduction by means of tin and hydrochloric acid?
6. Describe the separate action of chlorine, sulphuric acid, nitric acid, and nitrous acid on ethyl alcohol. (Punjab, B.Sc., 1924)

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Jaliamwale
Bagh
Mansoori

CHAPTER XVI

ETHERS

135. General. The ethers possess the same *general molecular formula* as the alcohols *viz.*, $C_nH_{2n+2}O$. Structurally they are regarded as the anhydrides of alcohols in the same sense as the metallic oxides are the anhydrides of metallic hydroxides.

Ethyl alcohol, C_2H_5OH

Ethyl ether, $C_2H_5.O.C_2H_5$

Sodium hydroxide, $NaOH$

Sodium oxide, Na_2O .

An ether is said to be *simple* or *mixed*, according as the two alkyl groups linked to the oxygen atom be identical or different. Thus diethyl ether, $C_2H_5.O.C_2H_5$, is a simple ether, while methyl ethyl ether, $CH_3.O.C_2H_5$, is a mixed ether.

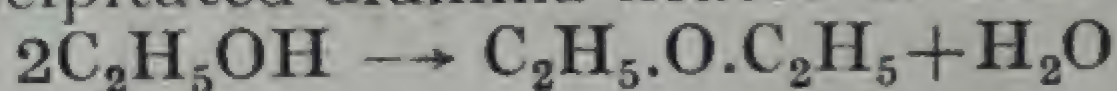
Ethers exhibit metamerism (Sec. 35):

136. Formation. Ethers may be prepared by the following general methods:—

(1) FROM ALCOHOLS:—

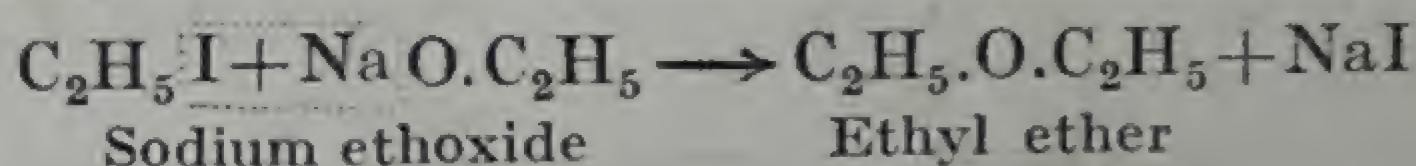
(i) *By heating with Concentrated Sulphuric Acid.* This reaction is of great practical importance, and will be described in detail in the case of ethyl ether.

(ii) *By Catalytic Dehydration.* In this method the alcohol vapour is passed over precipitated alumina heated at 240° to 260° .



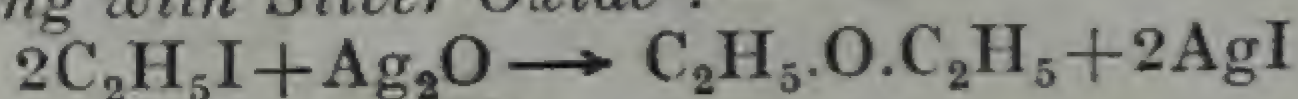
(1) FROM ALKYL HALIDES:—

(i) *By Heating with Sodium Alkoxides (Williamson's Synthesis):*



This method is of great interest, since it shows very clearly the structure of ethers. Moreover, it affords a simple method for synthesizing any desired ether, simple or mixed. Thus methyl ether may be obtained by heating a mixture of methyl iodide and sodium ethoxide or of ethyl iodide and sodium methoxide.

(ii) *By Heating with Silver Oxide:—*

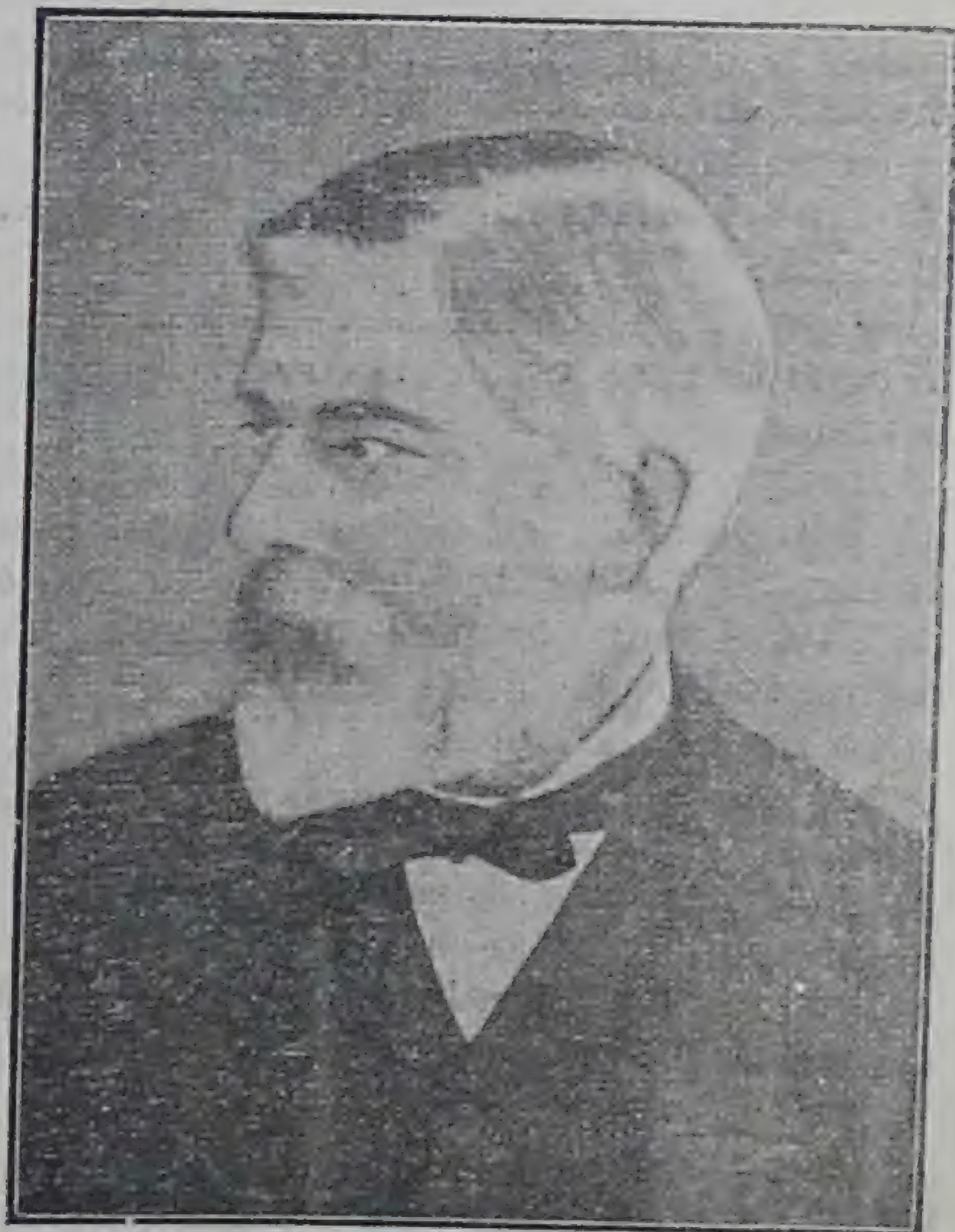


137. Physical Properties. With the exception of dimethyl ether, which is gaseous at ordinary temperatures, the aliphatic ethers are colourless, mobile, and volatile liquids having a pleasant

odour. They are highly inflammable and are lighter than water. Ethers dissolve in water to a very limited extent.

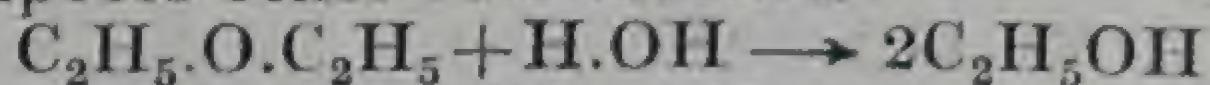
ALEXANDER WILLIAM
WILLIAMSON
(1824—1904)

an English chemist, was born in London on May 1st, 1824. In 1844, he joined Liebig's laboratory at Giessen, and, in 1885, was called to the chair of Practical Chemistry at the University College, London. Here he investigated the *etherification process*, and established the real nature of ether and its genetic relation to alcohol.

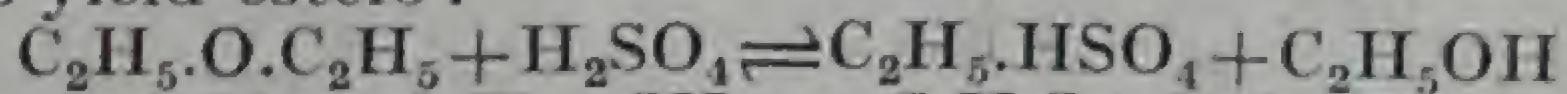


138. Chemical Properties. Chemically, ethers are far more inactive than alcohols, and are stable to metallic sodium, alkalies, and phosphorus pentachloride in the cold. The following are the chief reactions of ethers:—

1. *Hydrolysis.* Superheated water containing a little sulphuric acid slowly decomposes ether into alcohols:

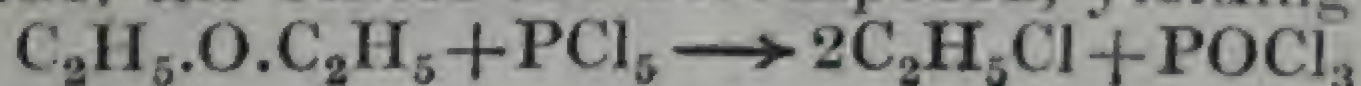


2. *Action of Concentrated Acids.* When heated with concentrated acids, ethers yield esters:



The excess of the acid may, of course, react with the alcohol produced, yielding a further quantity of the ester.

3. *Action of Phosphorus Pentachloride.* When heated with phosphorus pentachloride, the ethers are decomposed, yielding alkyl chlorides:



139. Constitution. The constitution of ethers as alkyl oxides follows from Williamson's synthesis, and is supported by their reactions.

140. Identification and Estimations. The alkyl radicals present in the ether can be ascertained by heating it with concentrated hydriodic acid, when the halogen combines with the *smaller* alkyl group. Thus methyl propyl ether yields methyl iodide and propyl alcohol :



When the reaction is over, the products are identified in the usual manner.

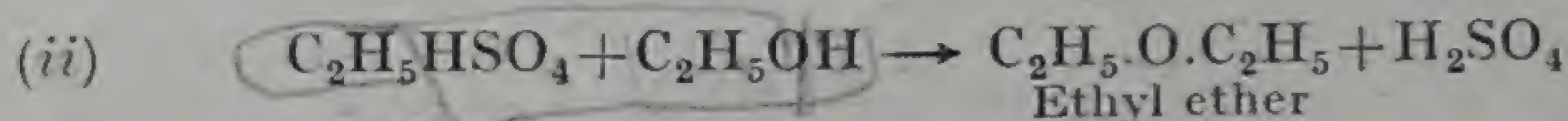
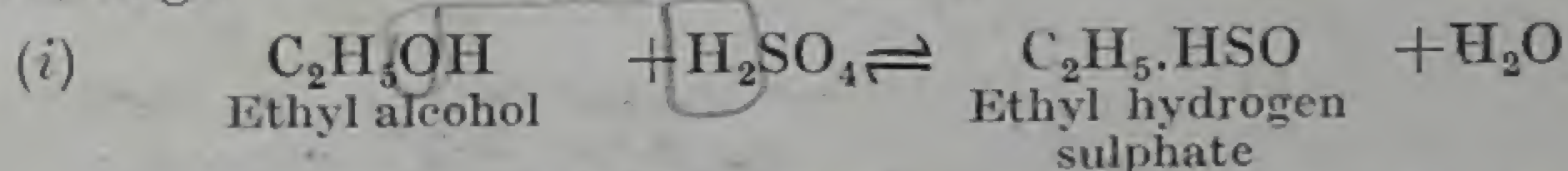
Many complex ethers (*e.g.*, *anethole* and *eugenol*) occur in nature as components of certain essential oils. These are mixed ethers containing (i) a methyl group, and (ii) a complex aromatic group. The methyl group or the methoxyl group in these compounds can be estimated by Zeisel's method, which consists in heating the compound with hydriodic acid :



The resulting alkyl iodide is passed into a solution of silver nitrate in 90 per cent alcohol, and the precipitated silver iodide is filtered and weighed. An alternative method consists in decomposing the alkyl iodide by heat, absorbing the iodine thus set free in an aqueous solution of potassium iodide, and titrating against standard thiosulphate.

141. Diethyl Ether, $\text{C}_2\text{H}_5.\text{O}.\text{C}_2\text{H}_5$. *Ethyl Ether*, or simply *Ether*. This is the most important member of the homologous series of ethers.

Preparation. Ether is prepared both technically and in the laboratory by heating a mixture of ethyl alcohol and concentrated sulphuric acid at 140° . The reaction has been shown to proceed in two stages :—



The ethyl hydrogen sulphate, produced in the first stage of the reaction, reacts with more of the alcohol producing ether and regenerating sulphuric acid. The latter then acts once again with a further quantity of alcohol, producing more of ethyl hydrogen sulphate and ether. The process is therefore, *continuous*, and theoretically a small amount

of sulphuric acid will etherify an unlimited quantity of alcohol. Actually, however, side reactions take place and the acid is gradually destroyed, owing to its reduction to sulphur dioxide.

Expt. 46. Preparation of Ether. The apparatus employed for the preparation of ether is shown in Fig. 67. A half-litre distillation flask is fitted with dropping funnel and a thermometer. Its side tube is attached to a long condenser, the lower end of which is fitted into the neck of a second distillation flask to act as the receiver. A long rubber tube is attached to the side tube of the receiver to carry off the ether vapour into the sink. This arrangement prevents the ether vapour from catching fire.

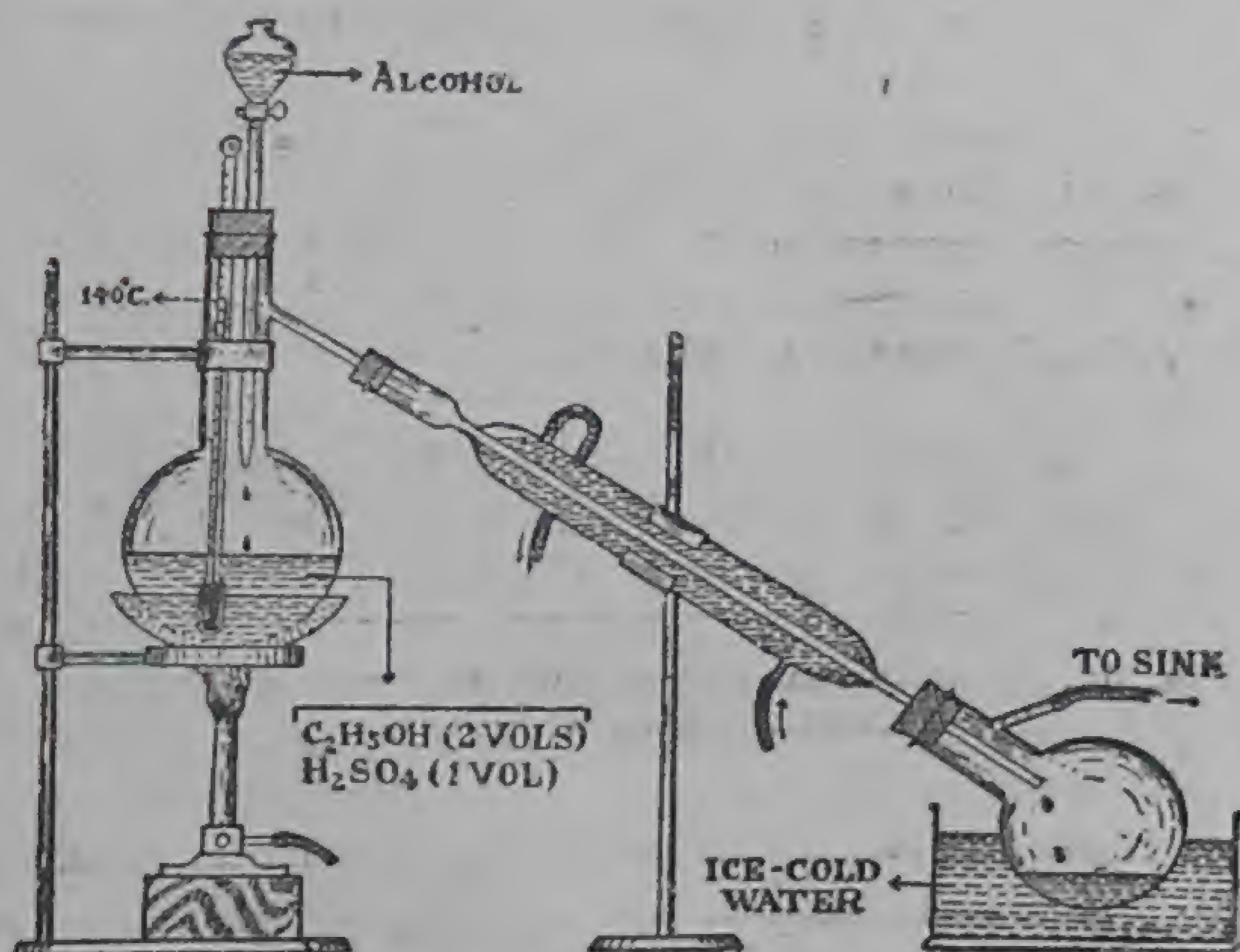


Fig. 67. Preparation of Ethyl Ether in the Laboratory.

50 c.c. of concentrated sulphuric acid are gradually added, with constant shaking, to 100 c.c. of alcohol contained in the distillation flask. The latter is then heated on a sand bath, until temperature rises to about 140° , when ether begins to distil over. Alcohol is now run in from the dropping funnel at nearly the same rate as that of the distillation, the temperature being maintained at 140° .

The distillate contains alcohol, water, and sulphur dioxide, in addition to ether. It is purified by shaking, in a separating funnel, first with a solution of sodium hydroxide to remove sulphur dioxide and then with water. The upper ethereal layer is separated and dried over anhydrous calcium chloride. It is then redistilled from a water bath, when pure ether passes over at 34° – 35° C.

The etherification of alcohol can be made really continuous by using, in the above process, syrupy phosphoric acid instead of concentrated sulphuric acid, as, unlike the latter, the former is not a reducible compound.

Manufacture. As already stated, ether is manufactured by the etherification of ethyl alcohol. Equimolecular proportions of ethyl

alcohol and concentrated sulphuric acid are introduced in a vessel provided with a closed coil through which superheated steam can be circulated (Fig. 68). The mixture is heated to about 140°C by means of superheated steam, and more alcohol is added at about the

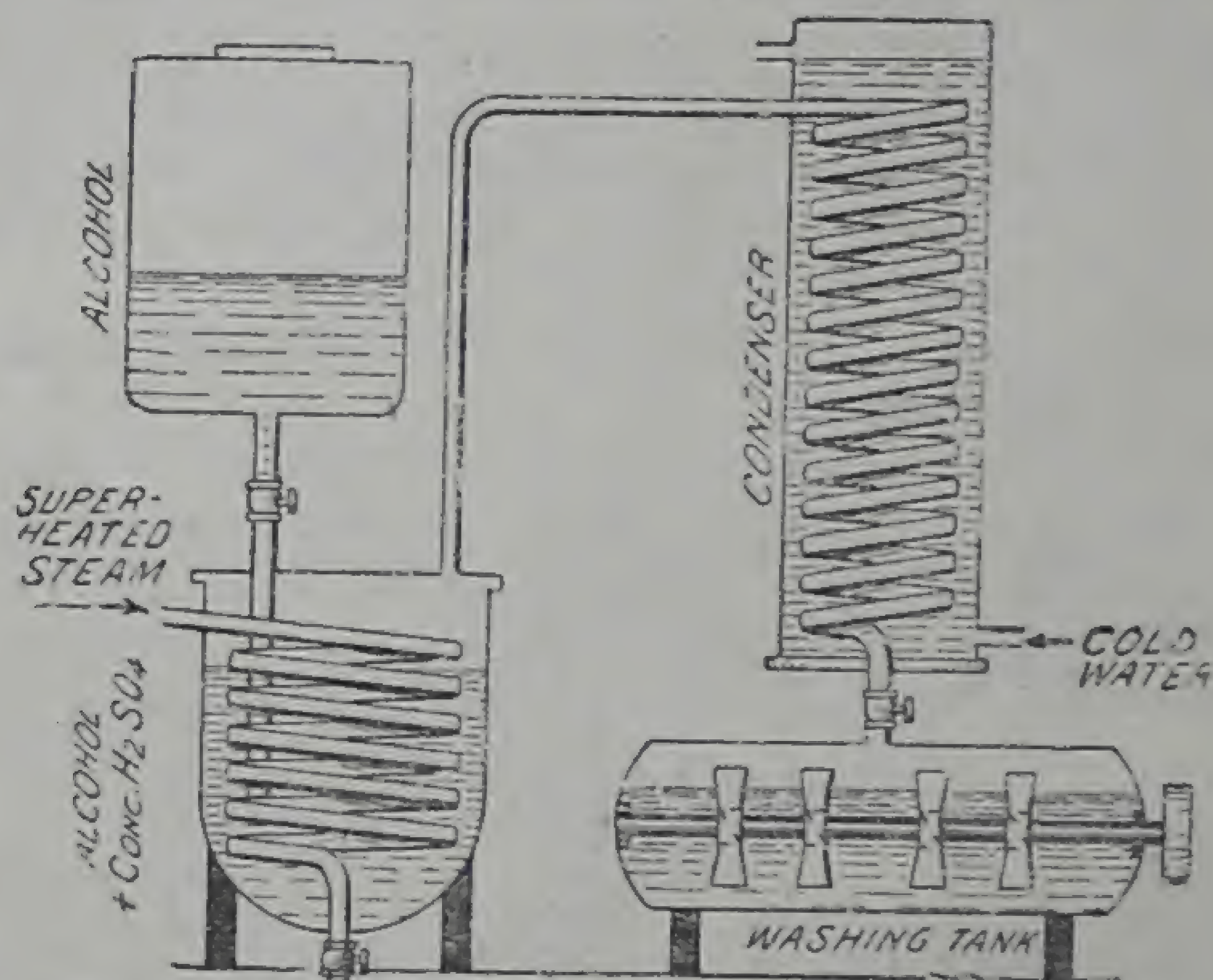
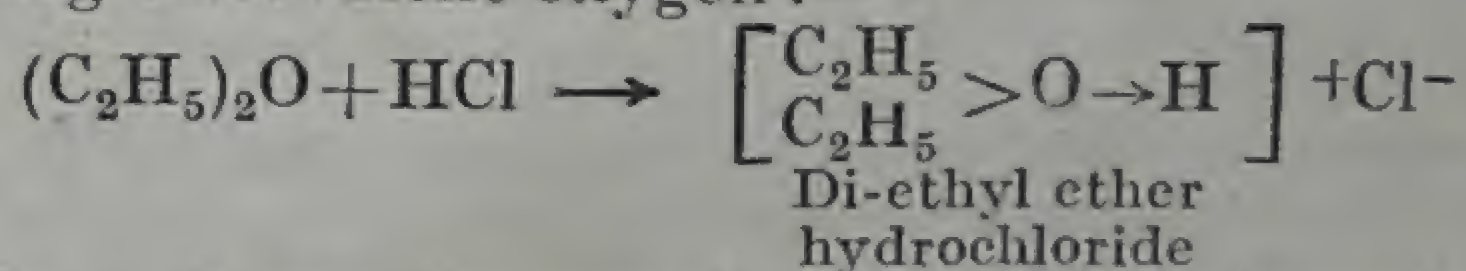


Fig. 68. Continuous Etherification Process for the Manufacture of Ether.

same rate at which ether distils over. The distillate is washed with a solution of sodium carbonate dried with anhydrous calcium chloride, and redistilled.

Properties. Ethyl ether is a colourless, mobile, and highly volatile liquid boiling at 35.5° . It is only slightly soluble in water (1 vol. in 11 vols at 25°). In aqueous hydrochloric acid, ether is far more soluble than in water. This is due to the formation of an oxonium salt containing tercovalent oxygen:—



Ethyl ether shows the usual chemical characters of ethers (Sec. 138).

Uses. (1) Ether is a very valuable *solvent* and crystallizing medium for many organic compounds, and is utilized for extracting aqueous solutions (Sec. 1). It is employed on a very large scale in the manufacture of collodion and chardonnet silk.

(2) It is the most frequently used as an *anæsthetic* in surgery.

(3) A mixture of alcohol and ether, is used in the place of petrol as a *motor fuel* (Sec. 122).

(4) Ether provides a very suitable *inert medium* for carrying out certain organic reactions, notably the Wurtz' reaction (Sec. 73) and the Grignard's reaction (Sec. 108B). In the preparation of phosphine, PH_3 , the air inside the flask is usually replaced by ether vapour (see a text-book of Inorganic Chemistry).

QUESTIONS

1. Give the general method of preparing aliphatic ethers, and describe their chief properties.

2. Describe in detail the laboratory method for preparing ethyl ether. Give an explanation of the reaction involved. To what important uses is ether put in the laboratory and technically?

3. The analysis of an organic substance gave the following results. 0.2115 gm. on combustion gave 0.4655 gm. CO_2 and 0.2533 gm. H_2O . The vapour density of the substance was 29.7. The compound failed to react with metallic sodium, and, on being distilled with hydriodic acid, it gave methyl iodide, ethyl iodide, and ethyl alcohol. What is the substance? [Ans. Methyl ethyl ether.]

4. An organic substance is found to contain $\text{C} = 52.2\%$. $\text{H} = 13\%$. $\text{O} = 34.8\%$. 0.069 gm. of the substance displaced 33.6 c.c. of air when measured at N.T.P. The substance reacts neither with sodium nor with phosphorus pentachloride in the cold. What is the substance? [Ans. Dimethyl ether, $(\text{CH}_3)_2\text{O}$]

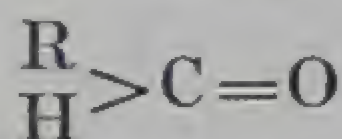
5. In a Zeisel's determination for methoxyl groups one gm. of a substance of the formula $\text{C}_4\text{H}_8\text{O}_2$ gave after treatment with red phosphorus, iodine and water, and the decomposition of the resulting methyl iodide with alcoholic silver nitrate 2.67 gm. of AgI . Calculate how many methoxyl groups are present in the molecule. (Punjab, B.Sc., Hons. 1914)

(Ans. One)

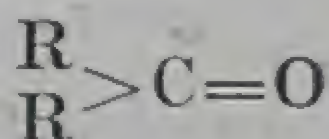
CHAPTER XVII

ALDEHYDES AND KETONES

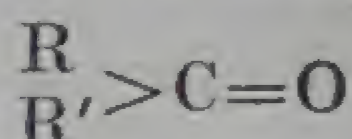
142. General Formulæ and Nomenclature. Aldehydes and ketones constitute two isomeric series of carbon compounds possessing the general molecular formula, $C_nH_{2n}O$. Both contain the divalent $>CO$ group, which in the case of aldehydes is linked on the one hand to an alkyl radical and on the other to hydrogen, while in ketones it is linked to two alkyl groups. If the two alkyl groups be identical, the ketone is termed a *simple* ketone, and if they are different, it is called a *mixed* ketone.



Aldehyde

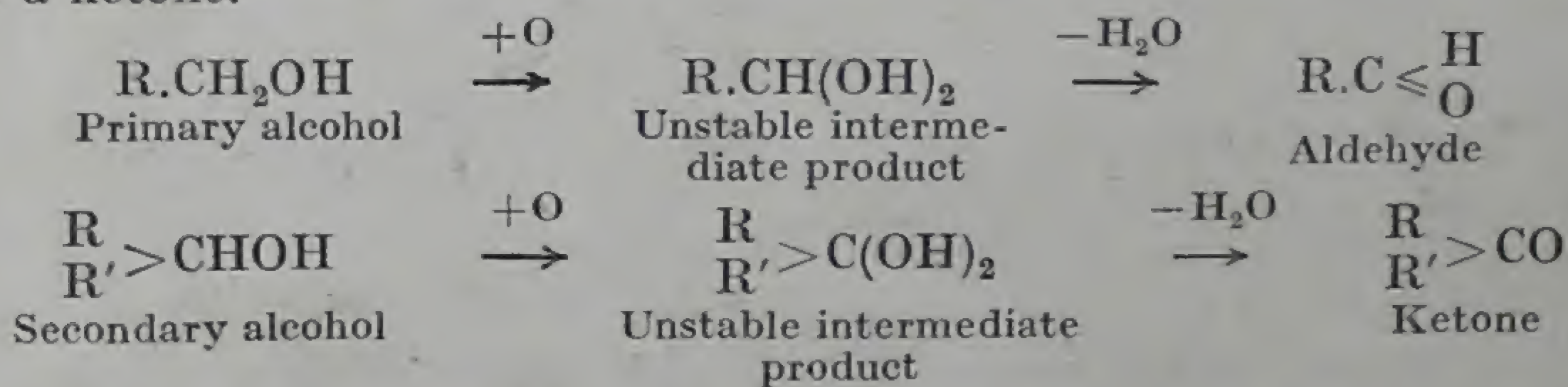


Simple ketone



Mixed ketone

Aldehydes and ketones are oxidation products of primary and secondary alcohols respectively, being derived from these by the removal of two hydrogen atoms. The change may be supposed to take place in two stages: In the first instance, an oxygen atom is added, with the production of a compound having two hydroxyls linked to the same carbon atom. This compound, since it is unstable, immediately loses a molecule of water, yielding an aldehyde or a ketone.



Aldehydes are usually named after the acid that they give rise to on oxidation, and ketones after the alkyl groups that they contain. Simple ketones are also named after the acid from which they may be obtained by the action of heat on its calcium salt (see below). The Geneva names of aldehydes and ketones are derived from those of the parent hydrocarbons by replacing the terminal *-e* by *-al* for aldehydes and by *-one* for ketones. Polyketones are distinguished as *diones*, *-triones*, etc. The following few examples illustrate the nomenclature adopted.

Properties. Acetone is a colourless liquid having a pleasant, peppermint-like odour. It boils at 56°C . It is perfectly miscible with water, alcohol and ether.

The reactions of acetone have already been described (Secs. 145 and 146).

Expt. 55. Preparation and Properties of Acetone. Heat 50 gm. of dry calcium acetate in a retort attached to a Liebig condenser (Fig. 72). Dilute the distillate, which contains some tarry matter, with an equal volume of water and then filter through a fluted filter to remove the tarry matter.

Show the presence of acetone in the aqueous solution obtained as above by the following tests :—

(1) **Legal's Test.** Take about 5 c.c. of the solution in a test tube, and about 1 c.c. of sodium hydroxide and then about 5 drops of a freshly prepared, solution of sodium nitroprusside (5 per cent). A ruby-red colour is produced which fades to yellow on standing.

Repeat the above test, and acidify the solution at once with acetic acid. A purple red colour is produced.

(2) **Iodoform Reaction.** Acetone gives iodoform reaction in the cold : Take about 2 c.c. of dilute acetone solution, add about 5 drops of sodium hydroxide, and then add a decinormal iodine solution, drop by drop, until the liquid becomes faintly yellow. There occurs an immediate separation of iodoform.

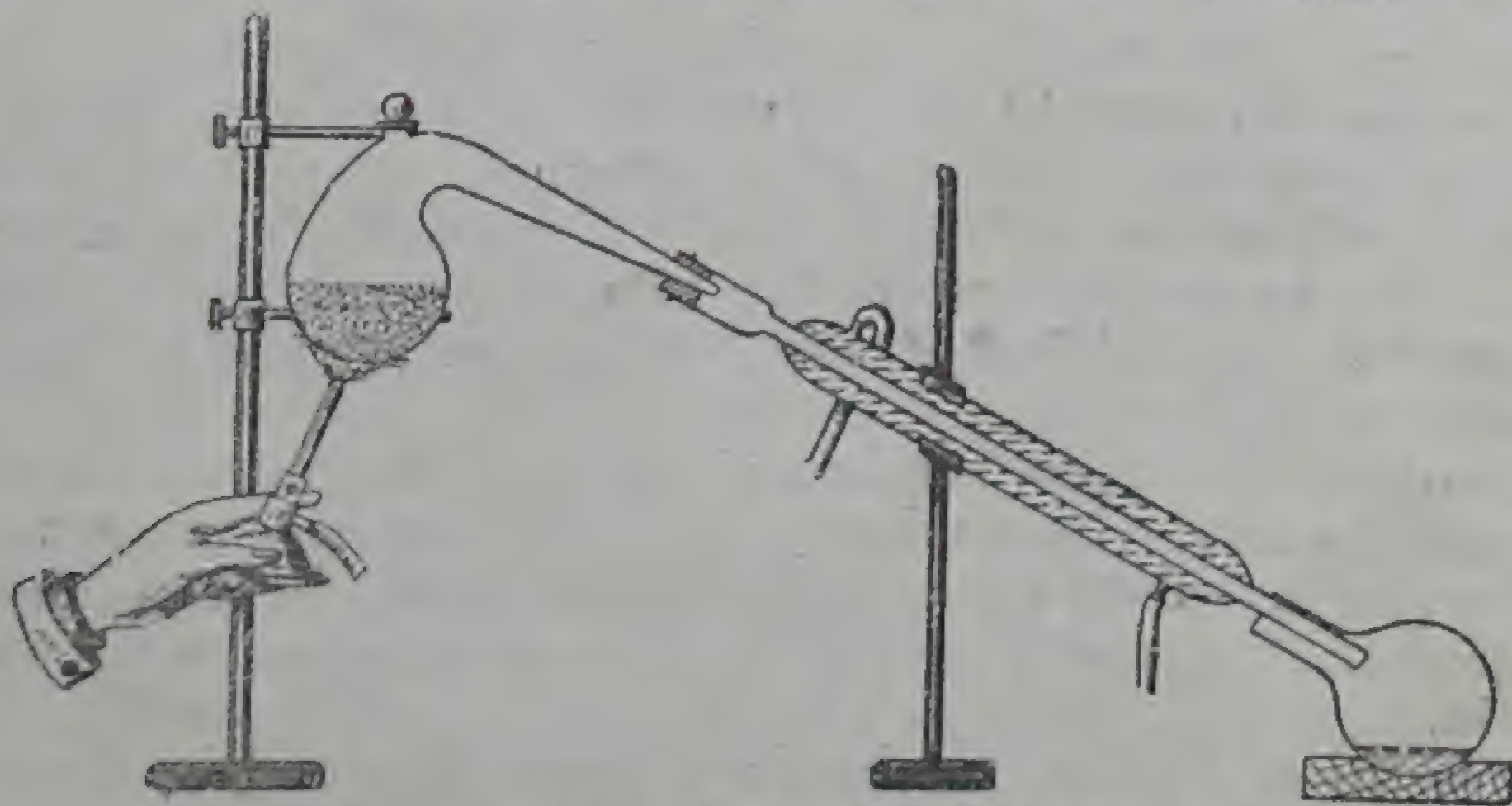


Fig. 72. Preparation of Acetone from Calcium Acetate.

Repeat the above test, using ammonia instead of sodium hydroxide. On adding iodine, drop by drop, a small amount of a black precipitate of nitrogen iodide is formed. Allow to stand, or warm. The precipitate disappears and iodoform is produced. This reaction serves to distinguish acetone from ethyl alcohol.

(3) **Formation of Indigo.** Dissolve a small quantity of *o*-nitrobenzaldehyde in about 1 c.c. of acetone, stir the solution into about 100 c.c. of water containing a little sodium hydroxide. Notice the rapid formation of indigo blue.

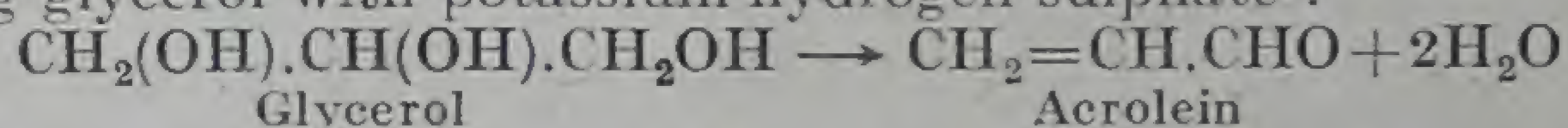
Uses. (1) Acetone is an important solvent, and is used in the preparation of high-class varnishes, cordite, and collodion, and for storing acetylene. It is also employed for extracting resins from wood and for making paint and varnish removers.

(2) It is used in the preparation of chloroform, iodoform, sulphonal, ionone, and synthetic rubber.

UNSATURATED ALDEHYDES AND KETONES

153. General. Unsaturated aldehydes show the same chemical reactivity as saturated aldehydes. Further, on account of the presence of double and triple bonds, they also undergo the addition reactions characteristic of the unsaturated hydrocarbons from which they are derived.

154. Acraldehyde, Acrolein, Propenal. $\text{CH}_2=\text{CH}.\text{CHO}$. This is the simplest unsaturated aldehyde. It is obtained by removing the elements of water from glycerol, this being usually effected by distilling glycerol with potassium hydrogen sulphate :



Expt. 56. Heat a mixture of glycerol with about one-fifth its weight of crystallized potassium bisulphate. The vapour evolved has an unpleasant odour and attacks the eyes. Notice the action of the vapour on a drop of bromine water held on a glass rod.

Properties. (1) Acrolein is a colourless oily liquid, having an extremely pungent odour, hence the name (*acer*, pungent; *oleum* oil). The irritating, unpleasant odour produced when a vegetable-oil-lamp or a tallow candle is put out is due to the formation of this substance. When brought in contact with the skin, it produces sores, and its vapour causes a plentiful flow of tears. It boils at 52° , and is difficultly soluble in water.

(2) Like other aldehydes, acrolein gives the silver mirror test and Schiff's magenta test. Its tendency to polymerize is so great that it usually changes in a short time to an amorphous, brittle substance called disacryl. It is readily oxidized, even on exposure to air, to form acrylic acid.

(3) In addition to the aldehydic characters, acrolein shows the behaviour of an unsaturated compound. Thus, with bromine it gives the dibromide $\text{CH}_2\text{Br}.\text{CHBr}.\text{CHO}$. Catalytic hydrogenation in the presence of nickel at 50° to 60° converts it into propaldehyde, $\text{CH}_3\text{CH}_2.\text{CHO}$. With hydrobromic acid acraldehyde yields β -bromopropaldehyde, $\text{CH}_2\text{Br}.\text{CH}_2.\text{CHO}$ (compare action of HBr on acrylic acid. (Sec. 176). Acrolein combines with *two* molecules of sodium bisulphite instead of one. When the resulting addition compound is treated with acids acrolein is *not* regenerated, only one molecule of the bisulphite being eliminated. This shows that the second molecule of sodium bisulphite must have been added at the double bond.

155. Crotonaldehyde, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CHO}$. As already mentioned (*p.* 213), this substance is obtained from aldol by the elimination of water. It is a pungent-smelling liquid (*b.p.* 105°) closely resembling acrolein in its chemical behaviour. On oxidation by means of silver oxide, it yields solid crotonic acid, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{COOH}$.

***155A. Citral or Geranial.** This is a di-olefinic aldehyde characterized by a fragrant odour. It is 3 : 7-dimethyl- $\Delta^{2:6}$ -octadiene-1-al, $(\text{CH}_3)_2\text{C}:\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3):\text{CH}\cdot\text{CHO}$, and is closely related to geraniol (Sec. 139). On oxidation it yields geranic acid.

Citral occurs in various essential oils, notably those of orange rind, lemon-grass and certain species of eucalyptus. It is used as a lemon aroma and in the manufacture of ionone.

DIALDEHYDES AND DIKETONES

***155-B. General.** Dialdehydes and diketones are of considerable interest, as they are valuable starting-points for the syntheses of a variety of cyclic compounds. The dialdehydes may be obtained by Rosenmund's method, *i.e.*, by the reduction of corresponding acid chlorides by means of hydrogen in the presence of finely divided palladium.

According to the relative positions of the two CO groups, diketones are classified as α - or 1 : 2-diketones, β - or 1 : 3-diketones, and γ - or 1 : 4-diketones. According to the Geneva nomenclature, diketones are named after the corresponding hydrocarbons by using the termination -dione. The α -diketones are yellow, volatile liquids having a pungent smell, while β - and γ - compounds are colourless, pleasant-smelling liquids.

***155-C. Glyoxal, Oxaldehyde, Diformyl,** $\begin{array}{c} \text{HC}=\text{O} \\ | \\ \text{HC}=\text{O} \end{array}$. When ethylene glycol, ethyl alcohol or acetaldehyde is carefully oxidized with nitric acid, a polymer of glyoxal, $[(\text{CHO})_2]_n$, called poly-glyoxal¹, is obtained. When this is heated with phosphorus pentoxide, the monomeric glyoxal results.

Glyoxal is a yellow liquid (freezing-point 15° ; *b.p.* 51°). The vapour of glyoxal has an intense emerald green colour; on condensation, the vapour yields at first a green liquid. This substance is unstable, and, even when kept in a strong freezing mixture, rapidly polymerizes to para-glyoxal, an insoluble modification of unknown molecular weight.

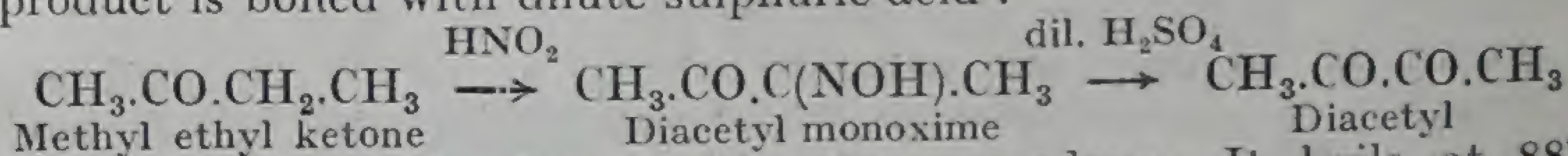
Glyoxal possesses the properties of an aldehyde. It reduces ammoniacal silver solution, and combines with two molecules of

¹ An amorphous substance, readily soluble in alcohol and ether.

sodium bisulphite to form the crystalline glyoxal sodium bisulphite, $C_2H_2O_2 \cdot 2NaHSO_3 \cdot H_2O$. It is by means of this derivative that glyoxal is usually isolated. Glyoxaloxime melts at 178° and the phenylhydrozone at 175° .

When treated with concentrated ammonia, glyoxal forms a cyclic base, called glyoxaline, which has the formula $\begin{array}{c} HC-NH \\ || \\ HC-N \end{array} \geq CH$. It melts at 90° and boils at 263° . Glyoxaline is of interest in connection with the constitution of the alkaloid pilocarpine.

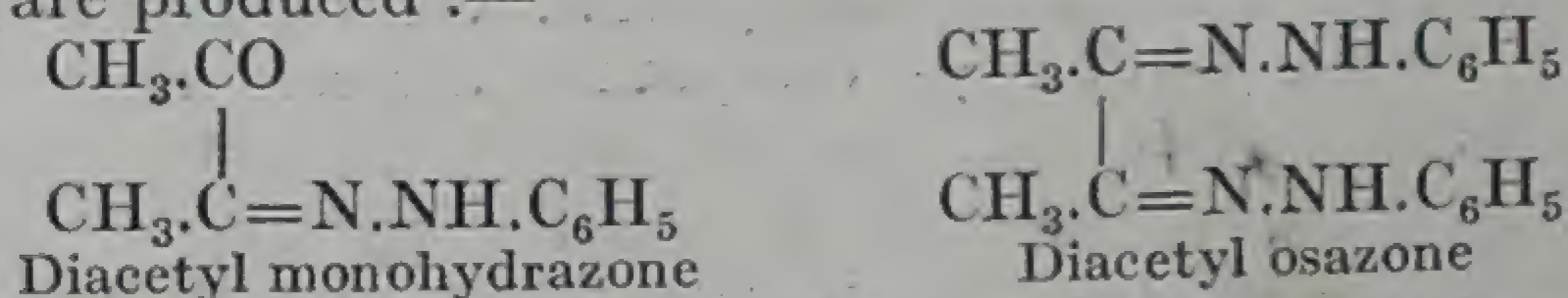
***155-D. Diacetyl, Butane-dione, $CH_3 \cdot CO \cdot CO \cdot CH_3$.** Diacetyl is the simplest α -diketone. It is prepared from methyl ethyl ketone *via* its monoxime. The ketone is treated with nitrous acid and the product is boiled with dilute sulphuric acid :—



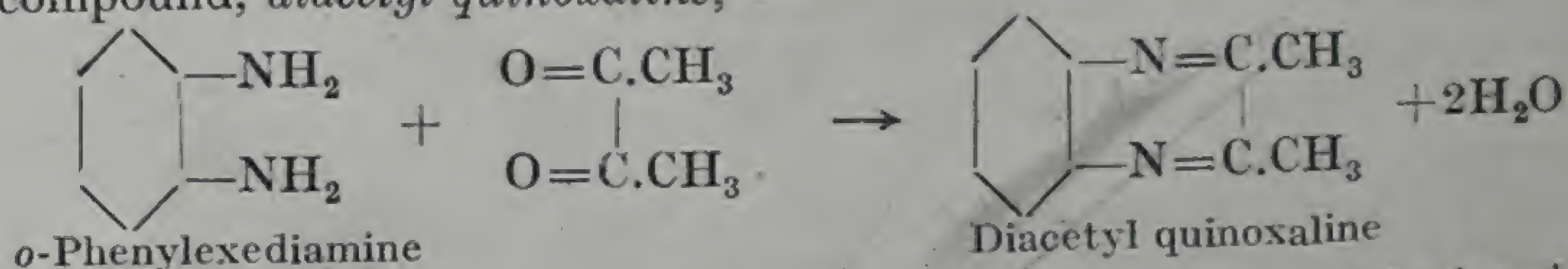
Diacetyl is a yellow liquid with a pungent odour. It boils at 88° to give a vapour having the colour of chlorine. Its more important reactions are :—

1. With hydroxylamine, it forms the monoxime, $CH_3 \cdot CO \cdot C(NO \cdot H) \cdot CH_3$, and the dioxime, $CH_3 \cdot C(NO \cdot H) \cdot C(NO \cdot H) \cdot CH_3$.

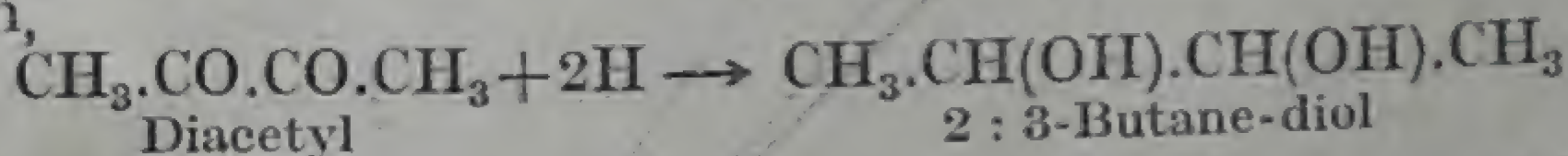
2. With phenylhydrazine, the monohydrazone and the dihydrazone (*isazone*) are produced :—



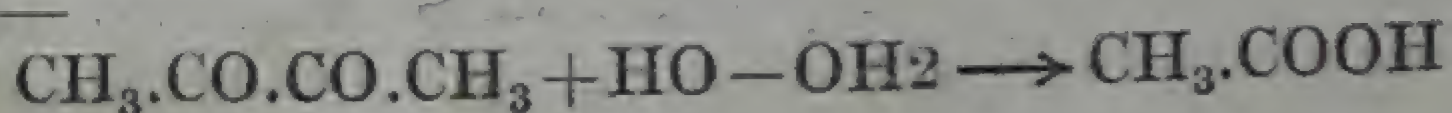
3. When treated with *o*-phenylene diamine, it forms the cyclic compound, *diacetyl quinoxaline*,



4. In the presence of fermenting yeast it undergoes biochemical reduction,



5. Hydrogen peroxide decomposes diacetyl into two molecules of acetic acid :—

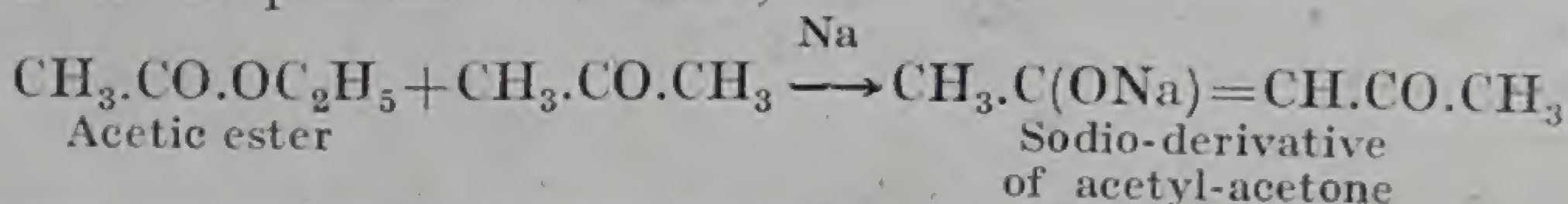


Dimethyl glyoxime is an important reagent, and is employed for the detection and gravimetric estimation of nickel and palladium, and also for the detection of bismuth.

Expt. 56A. Place a drop of a dilute solution of a nickel salt on a piece of filter paper, and on to it put one drop of 1 per cent alcoholic dimethyl glyoxime and then a drop of dilute ammonia. The formation of a red spot or ring indicates the presence of nickel.

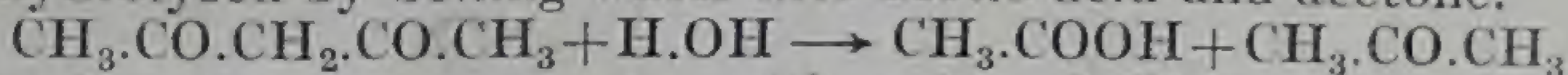
Expt. 56B. To a solution of bismuth chloride in hydrochloric acid add a little 1 per cent dimethyl glyoxime, and then strongly alkalify with ammonia. An intense yellow precipitate comes down in the presence of much bismuth, and a yellow colour is produced when traces of the metal are present.

*155-E. Acetyl-acetone, $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$. This is one of the β -diketones, and is prepared by condensing acetic ester with acetone in the presence of sodium,

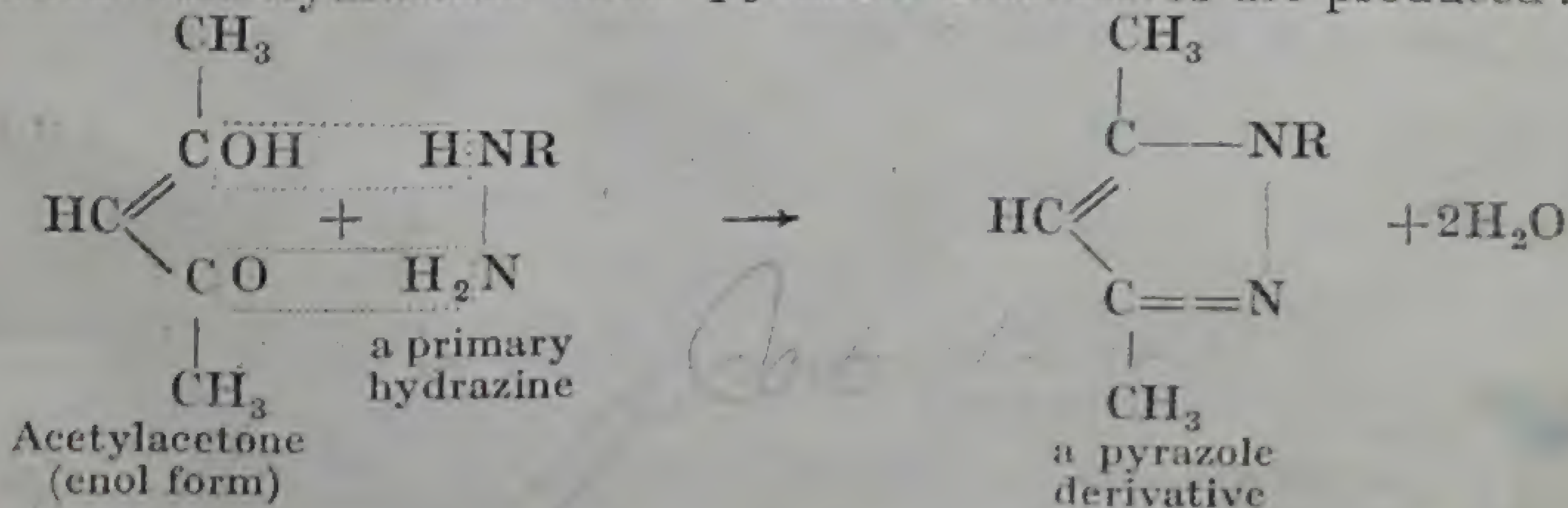


The resulting sodium compound is then converted into the insoluble cupric salt, from which acetyl-acetone is liberated by treatment with dilute sulphuric acid.

Acetyl-acetone is a colourless, pleasant-smelling liquid boiling at 137° . It is hydrolysed by boiling water into acetic acid and acetone.

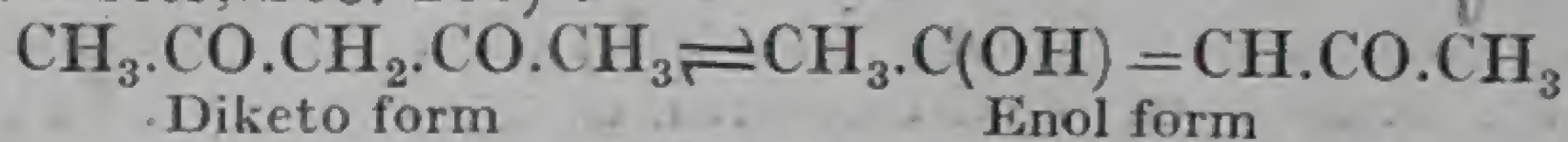


Acetyl-acetone, in common with other β -diketones, undergoes a large variety of condensations. Special mention may be made of its reaction with hydrazines when pyrazole derivatives are produced:—



Constitution. Acetyl-acetone, in common with other β -diketones, has been shown to exhibit keto-enol tautomerism (compare

Acetoacetic Ester, Sec. 266) :—

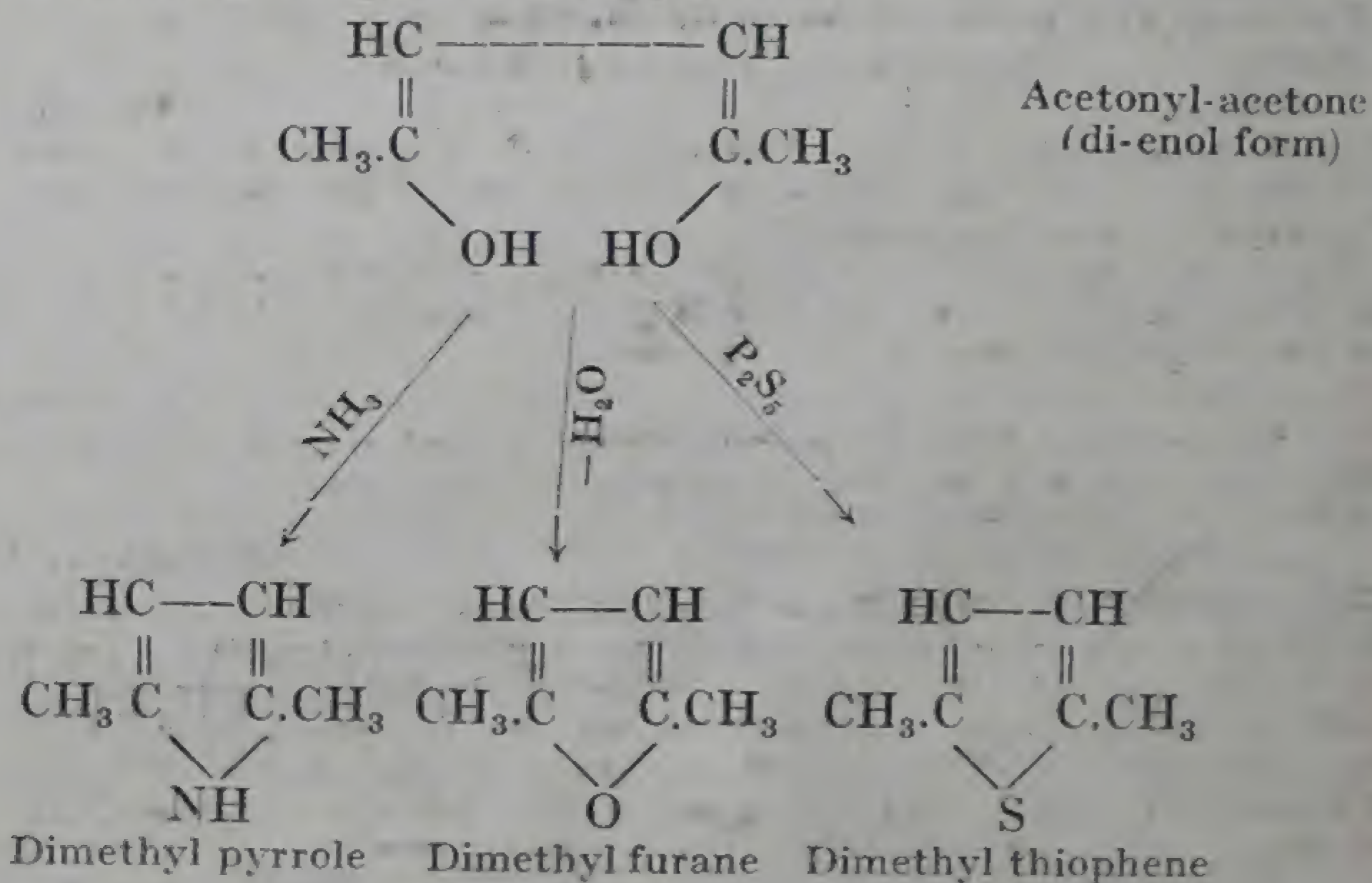


The power of the compound to form sodio-derivatives and other metallic salts proves the existence of the enol form. Many of these metallic derivatives are insoluble in water but soluble in organic solvents, such as benzene and chloroform.

The enol form of acetyl-acetone can be obtained in the pure state by crystallizing the equilibrium mixture from petroleum ether at low temperatures.

***155-F. Acetonyl-acetone, $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$, 2 : 5-Hexane-dione**, is an example of a γ -diketone. It may be conveniently prepared by boiling β -diaceto-succinic ester with sodium hydroxide. It is a colourless liquid with a pleasant smell, and is soluble in water, alcohol and ether. It boils at 191° under 750 mm.

Acetonyl-acetone, like other γ -diketones, is readily converted into derivatives of furane, thiophene and pyrrole :—



QUESTIONS

1. Name the groups of organic compounds to which the substance having the molecular formula $\text{C}_3\text{H}_6\text{O}$ may possibly belong. Give its possible constitutional formulæ, and describe experiments which you would perform to determine its constitution. (Punjab, Inter., 1926)
2. Give general methods of preparing aldehydes and the important reactions of the $-\text{HCO}$ group. (Punjab, B.Sc., Agr. 1933)
3. Describe the method you would adopt to prepare a pure sample of acetaldehyde in the laboratory. (Punjab, Inter., 1913)
4. How is formaldehyde prepared? In what important respects does it differ from acetaldehyde? Give its important uses.

5. Give the general methods for the preparation of ketones, and compare the reactions of these compounds with the reactions of aldehydes. (*Punjab, B.Sc., 1923*)

6. Give an account of the general methods by which aliphatic ketones can be prepared. What are their characteristic reactions?

How is acetone prepared commercially, and what are its uses?

(*Punjab, Inter., 1933*)

7. What are the main products obtained by the dry distillation of wood? How are these separated and purified? State to what commercial uses they are applied.

(*Punjab, B.Sc., 1924*)

8. Starting from acetone, show how you would prepare any five of the following:—

(a) Pinacone, (b) Phorone, (c) Mesitylene, (d) α -hydroxisobutyric acid, (e) Propylene, (f) Tertiary butyl alcohol.

(*Punjab, B.Sc., 1930*)

9. You are given a mixture containing ethyl alcohol, acetic acid and acetone. How would you proceed to identify these and separate them? Describe how you would proceed to prepare one compound from each of these substances?

(*Punjab, B.Sc., 1923*)

10. An organic compound gave the following results on analysis:

(a) 0.1475 gm. gave 0.088 gm. of carbon dioxide and 0.009 gram of water.

(b) 0.295 gm. gave 0.861 gm. of silver chloride.

(c) 0.1475 gm. displaced 24.6 c.c. of air at 76 cm. at 27°C.

The compound on treatment with NaOH solution gave chloroform as one of the products of decomposition. Assign a structural formula to the compound.

(*Bombay, Inter., 1932*)

11. A compound of carbon, hydrogen, and oxygen gave the following results: 0.146 gm. gave 0.374 gm. CO_2 and 0.154 gm. H_2O , and the vapour density determination gave the value 42.

The compound reacts with hydroxylamine and with phenylhydrazine, but not with acetyl chloride; on oxidation it gives a mixture of acetic acid and propionic acid with traces of other acids. Determine the molecular and structural formulae of the compound?

(*Punjab, B.Sc., 1933*)

12. A ketoxime, on analysis, was found to possess the following composition. Carbon, 55.2; hydrogen, 10.3; nitrogen, 16.1 per cent.

What is the formula of the compound and from what ketone is it derived?

(*Board of Education, 1931*)

13. A substance containing of C, H and O only, gives on analysis $\text{C}=68.19\%$ and $\text{H}=13.64\%$. When gently oxidized, it is converted into a substance which gives $\text{C}=69.77\%$ and $\text{H}=11.63\%$. The latter on further oxidation under suitable conditions gives a mixture which on analysis is found to consist of saturated fatty acids containing one, two, three, and four atoms of carbon per molecule, but none of the higher acids. Suggest a constitutional formula for the substance and describe the tests you would employ to confirm it.

(*Pembroke College, Cambridge*)

ANSWERS

10. Chloral CCl_3CHO .

11. Methyl propyl-ketone $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$.

12. $\text{CH}_3 > \text{C} : \text{NOH}$: from methyl-ethyl ketone.

13. The secondary alcohol, $\text{CH}_3\text{CHOH}\cdot\text{C}_3\text{H}_7$, yields the ketone $\text{CH}_3\text{CO}\cdot\text{C}_3\text{H}_7$.

CHAPTER XVIII

MONOCARBOXYLIC ACIDS

156. General. The characteristic group present in the carboxylic acids is the carboxyl group,—COOH. These acids may be regarded as derived from the hydrocarbons, and represent the final stage in the oxidation of the methyl group of the hydrocarbon molecule, the intermediate stages being represented by primary alcohols and aldehydes. The relationship between these compounds will be clear from the following examples :—

H.CH_3 Methane	$\text{H.CH}_2\text{OH}$ Methyl alcohol (Methanol)	H.CHO Formaldehyde (Methanal)	H.COOH Formic acid (Methane acid)
$\text{CH}_3.\text{CH}_3$ Ethane	$\text{CH}_3.\text{CH}_2\text{OH}$ Ethyl alcohol (Ethanol)	CH_3CHO Acetaldehyde (Ethanal)	$\text{CH}_3.\text{COOH}$ Acetic acid (Ethane acid)

1. SATURATED MONOCARBOXYLIC ACIDS

The saturated monocarboxylic acids are usually called fatty acids as the higher members of this series occur as glyceryl esters in fats and oils.

157. Nomenclature. The names of the fatty acids all end in *ic*, and generally indicate their source of preparation or the number of carbon atoms in the molecule. The Geneva names are derived from the parent hydrocarbon by the addition of the word "acid".

The following examples illustrate the nomenclature, the Geneva names being given in italics :

H.COH Formic acid (<i>Methane acid</i>)	$\text{CH}_3.\text{COOH}$ Acetic acid (<i>Ethane acid</i>)	$\text{C}_2\text{H}_5.\text{COOH}$ Propionic acid (<i>Propane acid</i>)
$\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{COOH}$ <i>n</i> Butyric acid or Ethyl acetic acid (<i>Butane acid</i>)	$(\text{CH}_3)_2\text{CH.COOH}$ Isobutyric acid or Dimethyl acetic acid (<i>2-Methyl propane acid</i>)	
	$\text{CH}_3\text{CH}_2.\text{CH}(\text{CH}_3).\text{COOH}$ α -Methyl butyric acid or Methyl-ethyl-acetic acid (<i>2-Methyl-butane acid</i>)	

Lead acetate or *sugar of lead*, $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$, and *basic lead acetate*, $\text{CH}_3\text{COO} \cdot \text{Pb} \cdot \text{OH}$, are used in the manufacture of lead preparations (e.g., "white lead"). A solution of lead acetate in water is something used under the name "lead lotion" as an external application in cases of sprains, etc. Basic copper acetate, $\text{CH}_3\text{COO} \cdot \text{Cu} \cdot \text{OH}$, technically known as *verdigris*, is used in the manufacture of green paint. Normal acetates of *aluminium*, *chromium*, *iron* and *copper* are largely employed as mordants.

166. Separation of Acetic Acid and Formic Acid
This is based on the solubility of lead and magnesium acetates in alcohol, the formates of these metals being insoluble. The mixture is neutralized with litharge, or magnesium carbonate, and the solution concentrated. Alcohol is then added, whereby the formate is precipitated. The two salts are then separately decomposed to get the free acids.

[Love RM no. 11 2nd Year Impossible]
167. Propionic Acid, Methyl Acetic Acid, $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{COOH}$.
This acid occurs in crude pyroligneous acid. It can be most readily obtained by the oxidation of propyl alcohol with potassium dichromate and sulphuric acid. It boils at 141° , and mixes with water in all proportions. From the aqueous solution it can, however, be "salted out" as an oily layer by the addition of solid calcium chloride and other salts.

168. Butyric Acids, $\text{C}_3\text{H}_7\text{COOH}$. There are two isomeric butyric acids, both of which are found in nature :

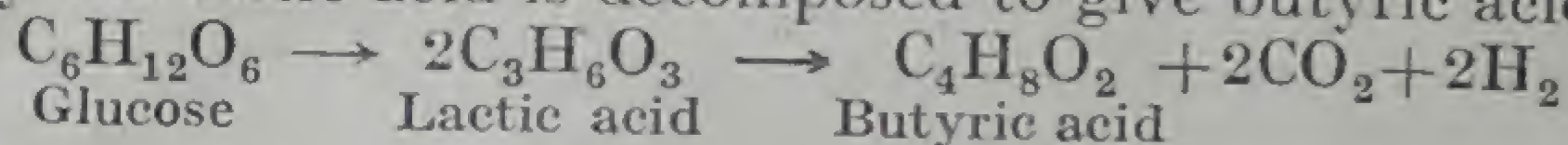
(1) *n*-Butyric acid, *Ethyl-acetic Acid*, $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$. This acid occurs as the glyceryl ester in butter to the extent of about 7 per cent, and in the free state in perspiration.

The acid is prepared by the butyric fermentation of saccharine or starchy materials, which is brought about by the combined action of the *lactic bacilli* and the *butyric bacilli*. The latter consists of slender rods in active movement.

A solution of starch or glucose is prepared, and to this some sour milk (which contains lactic ferment) and putrid cheese (which contains butyric ferment) are added. Some chalk or zinc carbonate is also added to keep down the hydron concentration of the fermenting liquid (as excessive acidity is ruinous to the growth of the ferments) and also a little tartaric acid, ammonium phosphate, and magnesium sulphate, in order to stimulate the growth of the ferments. The butyric acid, as soon as produced, is neutralized by the calcium or zinc carbonate present. The resulting solution containing calcium or zinc butyrate, is filtered, evaporated, decomposed with hydrochloric acid, and butyric acid separated by distillation.

During the above process of fermentation, the starch is first converted into glucose. The latter then undergoes lactic fermentation (*q.v.*):

and finally the lactic acid is decomposed to give butyric acid.



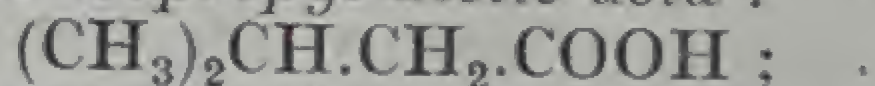
n-Butyric acid is an oily liquid (*b.p.* 163°), having an unpleasant smell of rancid butter. It is used in the manufacture of esters.

The calcium salt of *n*-butyric acid shows the peculiar behaviour of being *less* soluble in hot water than in cold. The fact is utilized for distinguishing the normal butyric acid from isobutyric acid, the calcium salt of the latter behaving normally, *i.e.*, it is more soluble in hot water than in cold.

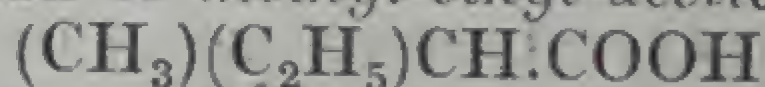
(2) **Isobutyric Acid**, *Diethyl-acetic Acid*, $(\text{CH}_3)_2\text{CH}.\text{COOH}$. This acid is found in the free state, or as esters, in many plants. It is prepared by the oxidation of isobutyl alcohol, $(\text{CH}_3)_2\text{CH}.\text{CH}_2\text{OH}$. It is an oily liquid, boiling at 154°. It differs from the normal acid in being not miscible with water and in the solubility of the calcium salt (*see above*).

169. Valeric Acids, $\text{C}_4\text{H}_9.\text{COOH}$. Of the four isomeric valeric acids the two more important are :

(1) **Isovaleric acid** or *isopropyl-acetic acid* :



(2) **Active valeric acid** or *methyl-ethyl-acetic acid*,



Both these acids occur in the plant all-heal, or valerian, and in angelica. A mixture of the acids obtained by distilling the macerated plants with water is known as *valeric acid* or *valerianic acid*. It is also obtained by oxidizing commercial amyl alcohol (Sec. 124) with potassium dichromate and sulphuric acid. It is an oily liquid boiling at about 175°.

The chief use of propionic, butyric and valeric acids is in the manufacture of esters, which are extensively employed in making artificial fruit flavours and lacquers.

170. Higher Homologues. Some higher members of the series having a normal chain and an even number of carbon atoms are found as glyceryl esters in fats and oils of animal and vegetable origin. Two of these *viz.*, palmitic acid, $\text{C}_{15}\text{H}_{31}.\text{COOH}$, melting at 62°, and stearic acid, $\text{C}_{17}\text{H}_{35}.\text{COOH}$, melting at 69°, are most important. A mixture of the two acids is manufactured on a large scale by hydrolysing fats, and is used in the manufacture of "stearine" candles (*see Chapter XX*). Soap is a mixture of the sodium salts of these acids.

II. UNSATURATED MONOCARBOXYLIC ACIDS

171. Oleic Acid Series. The monocarboxylic acids derived from olefine hydrocarbons have the general formula $\text{C}_n\text{H}_{2n-1}\text{COOH}$.

The most important number of the series is oleic acid, from which the series takes its name. A few important members of this series are :—

Acrylic acid, Propene acid, or Vinyl-formic acid, $\text{CH}_2=\text{CH}.\text{COOH}$

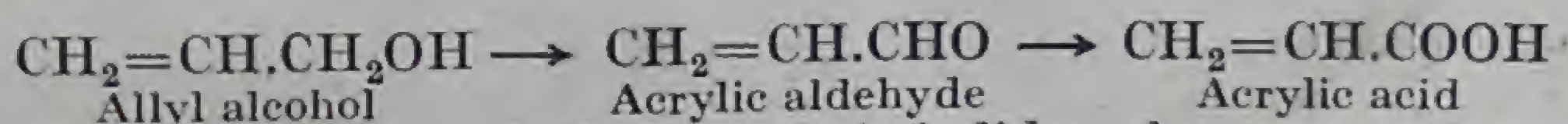
Vinyl-acetic acid, $\text{CH}_2=\text{CH}.\text{CH}_2.\text{COOH}$

Crotonic acid, β -methylacrylic acid, $\text{CH}_3.\text{CH}=\text{CH}.\text{COOH}$

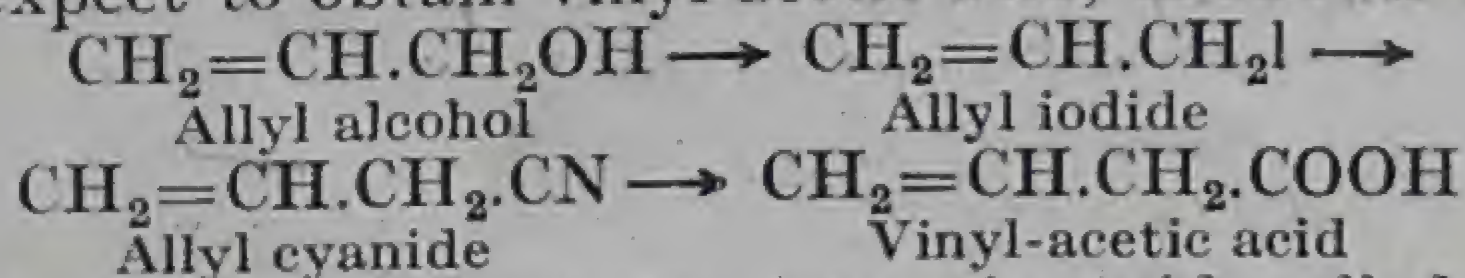
Oleic acid, $\text{CH}_3.(\text{CH}_2)_7.\text{CH}=\text{CH}.\text{CH}_2)_7\text{COOH}$.

172. General Methods of Formation. The acids of the oleic series may be obtained by methods analogous to those used in the case of fatty acids (Sec. 158), and also by the general methods for the preparation of unsaturated compounds. Of the methods given below, the first two belong to the former class and the last two to the latter :

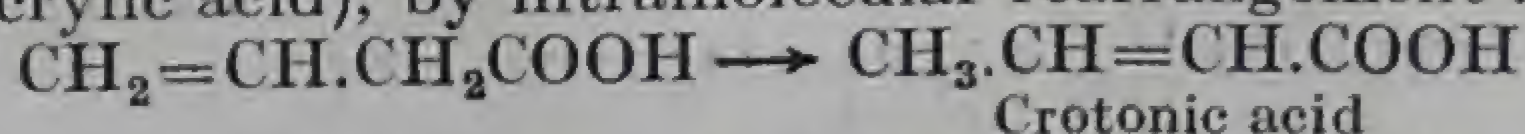
(1) By oxidizing the corresponding primary alcohols or aldehydes ; *e.g.*,



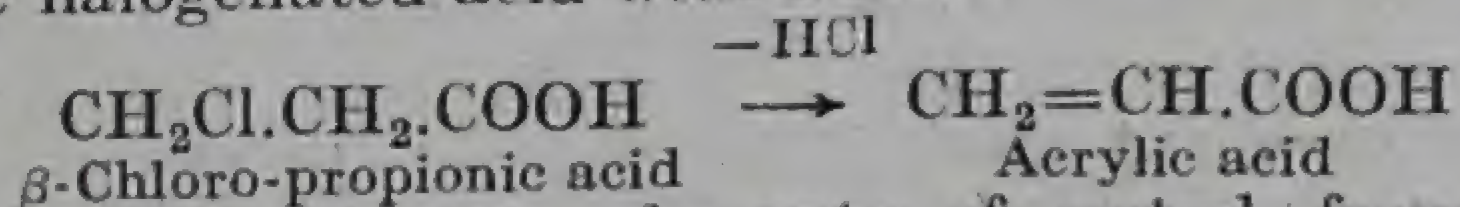
(2) From the olefine alcohols or their iodides, by converting them into the nitriles, which are then hydrolysed. Starting with allyl alcohol, we expect to obtain vinyl-acetic acid, as shown below :



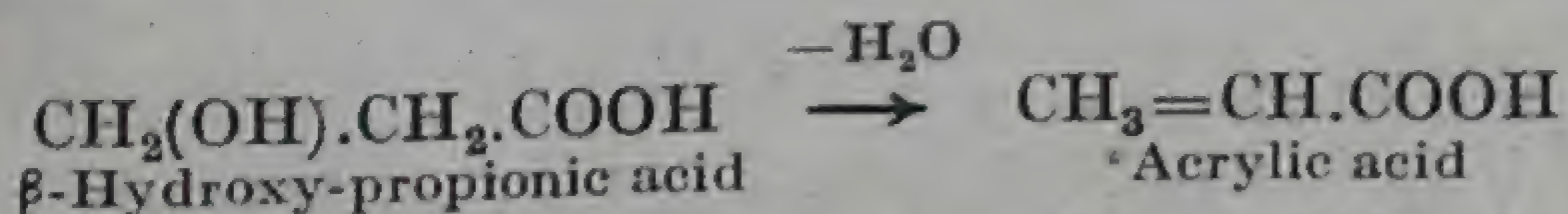
Actually, however, we get an isomeric acid, called crotonic acid (β -methyl-acrylic acid), by intramolecular rearrangement :



(3) By the removal of halogen hydride from monohalogen substitution products of fatty acids containing the halogen in the β -position to the carboxyl. The reaction may be effected sometimes by simply heating the halogenated acid with water.



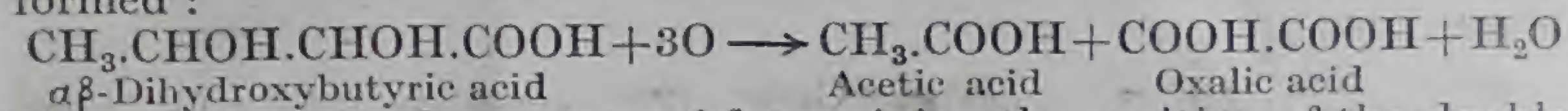
(4) By the removal of the elements of water¹ from a β -hydroxy acid ; *e.g.*,



173. Physical Properties. Apart from differences in melting-point, which are sometimes considerable, the physical properties of the acids of the oleic series are similar to those of the fatty series. The presence of the double bond increases the strength of the

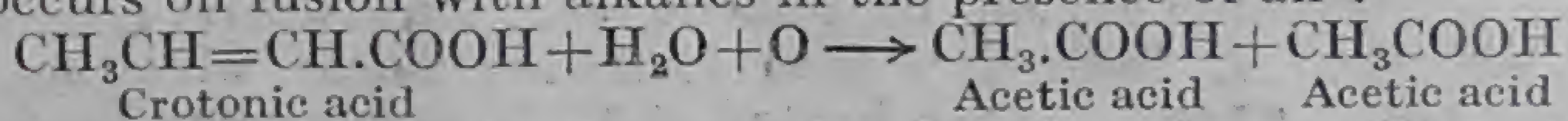
¹ This can be effected by simply heating the hydroxy acid.

formed :



The reaction affords a means of determining the position of the double bond in the molecule.

(5) A rupture of the molecule with the formation of saturated acids also occurs on fusion with alkalis in the presence of air :



The reaction, however, is of no use for locating the position of the double bond, as treatment with alkali has been shown to shift the double bond, if possible nearer to the carboxyl.

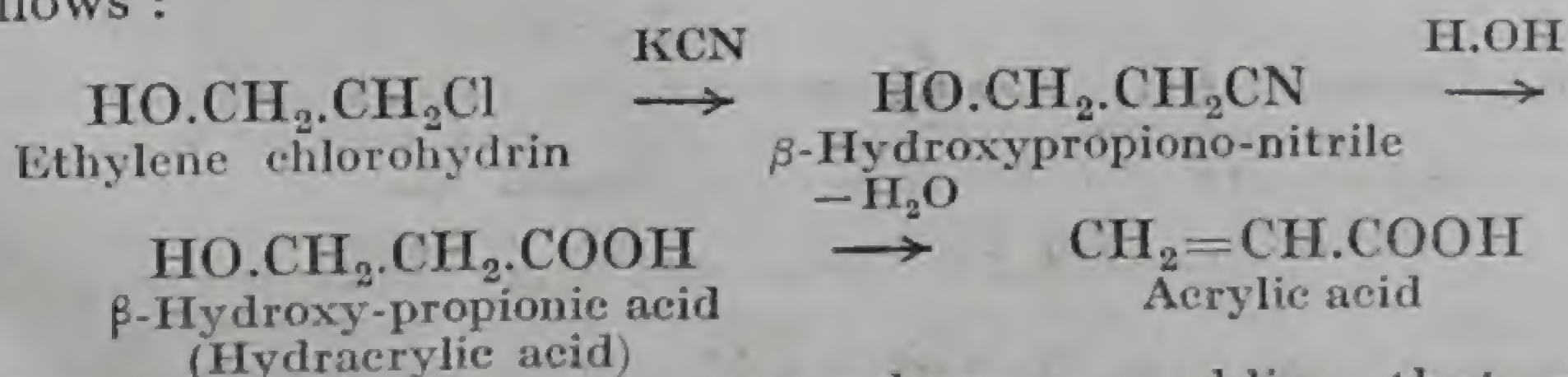
A similar shifting of position of the double bond is also sometimes observed, when an unsaturated cyanide is subjected to hydrolysis (compare, for example, the conversion of allyl cyanide into crotonic acid, *p.* 241).

175. Constitution. The determination of the constitution of an unsaturated acid involves the following points :

(i) The *nature of the chain*. This point is settled by hydrogenating the acid to the corresponding fatty acid.

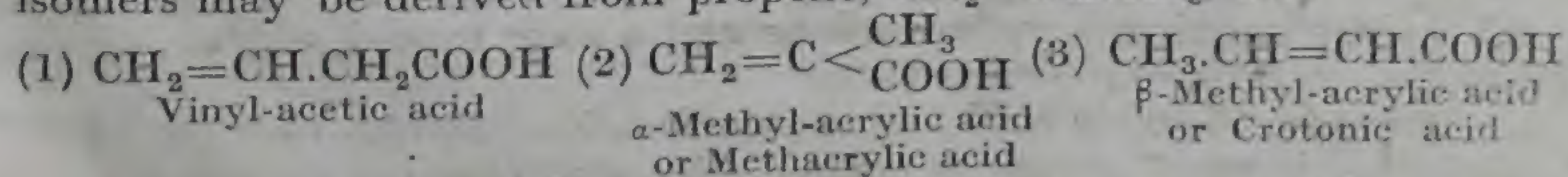
(ii) The *position of the double bond* in the molecule. This is done by oxidizing the acid (see above) or by ozonolysis (*p.* 137).

176. Acrylic Acid, Vinyl-formic Acid, $\text{H}_2\text{C}=\text{CH}.\text{COOH}$, Propene Acid. This acid is best prepared from ethylene chlorohydrin as follows :

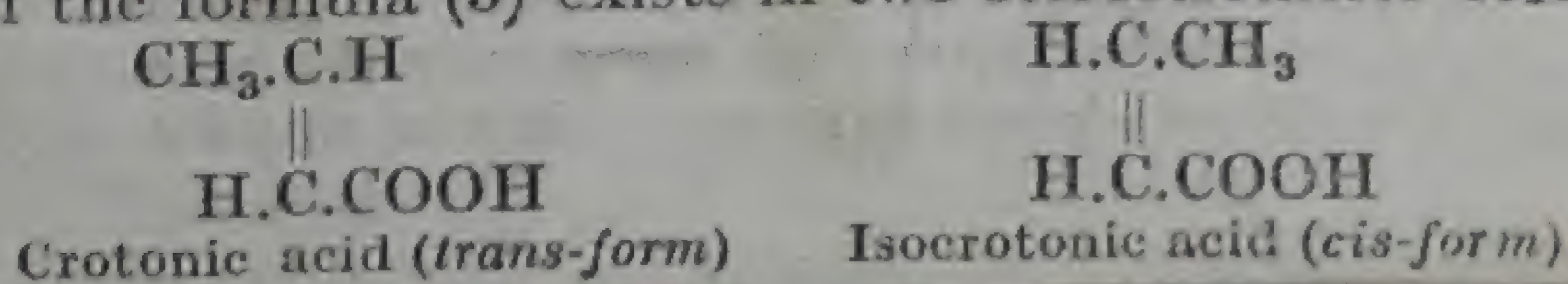


It is a liquid having a pungent odour, resembling that of acetic acid. It melts at 12.3° and boils at 140° . It shows all the reactions characteristic of this series (Sec. 174).

177. Acids of the Formula $\text{C}_4\text{H}_6\text{O}_2$. Three structural isomers may be derived from propene, $\text{CH}_2=\text{CH}.\text{CH}_3$, *viz.*



The acid of the formula (3) exists in two stereoisomeric forms, *viz.*



Thus there are four different acids of the formula $C_4H_6O_2$ belonging to this series.

178. Crotonic Acids. Ordinary crotonic acid or *solid crotonic acid* occurs in croton oil, and resembles acrylic acid closely. It may be obtained by the general methods, given above, or by the hydrolysis of allyl cyanide (*p.* 241). It melts at 72° and boils at 180° .

When solid crotonic acid in toluene solution is irradiated with ultra-violet light, it isomerizes into isocrotonic acid, which melts at 150° and boils at 169° . When heated at 170° to 180° in a sealed tube it passes back into solid crotonic acid.

Crotonic and isocrotonic acids are structurally identical. On reduction they *both* yield normal butyric acid, showing that the molecules contain no branched chain. With dilute potassium permanganate, each of them yields dihydroxybutyric acid, while with nitric acid a mixture of acetic acid and oxalic acid is produced (*pp.* 242-3). This proves the constitution of the acids. Solid crotonic acid, because of its being chemically more stable, is assigned the *trans*-formula, while the less stable isocrotonic acid is assumed to be the *cis*-compound.

✓ **179. Oleic Acid,** $CH_3.(CH_2)_7.CH=CH.(CH_2)_7.COOH$. This is the most important member of the present series. It occurs as the glyceryl ester, *triolein*, in fatty oils (such as olive oil or cotton seed oil), from which it is obtained as a by-product in the manufacture of stearine.

In the laboratory, oleic acid is best prepared from olive oil. The oil is saponified by boiling with an alkali solution. The water soluble alkali salts of the acids present are then converted into insoluble lead salts by double decomposition with lead acetate. These are filtered, washed with alcohol to remove unchanged olive oil and then shaken with ether, which dissolves only the lead oleate, the lead salts of stearic and palmitic acids being insoluble in ether. The ethereal solution is filtered, the ether evaporated, and the residue of pure lead oleate decomposed with pure dilute nitric acid, when oleic acid is liberated as an oily layer. This is separated, dried by means of fused calcium chloride, and then distilled under reduced pressure.

Oleic acid is a colourless liquid, having practically no odour or taste. It solidifies at 4° , yielding a mass of colourless needles, which melt again when the temperature rises to 14° . In contact with air, the acid rapidly acquires a yellow colour and a sour rancid odour, owing to oxidation.

When reduced, oleic acid yields stearic acid. Hence, like the latter compound, it must contain a normal straight chain of carbon atoms. Further, on oxidation with cold, dilute potassium permanganate solution, it yields a mixture of *nonylic acid* and *azelaic acid*. This shows that the double bond is situated in the middle of the chain :

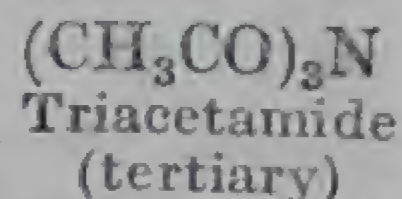
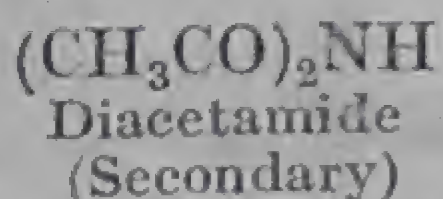
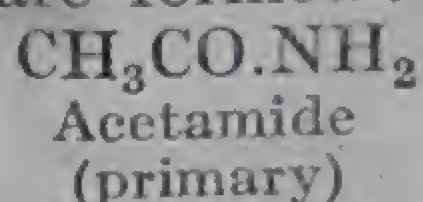
the dropping funnel, stir the mixture well with a glass rod, and close the retort with a glass stopper. Heat the retort with a luminous flame, kept in constant motion. When no more liquid collects in the receiver, add a little anhydrous sodium acetate to the collecting flask and re-distil, collecting the fraction passing at 135° to 140°.

Acetic anhydride is a colourless, non-fuming liquid having a pungent, acetic acid-like odour. It boils at 137°, and is heavier than water.

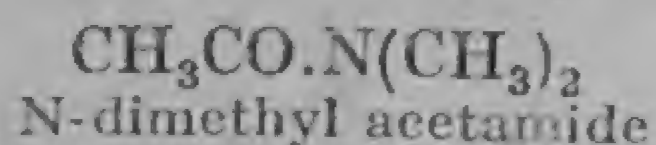
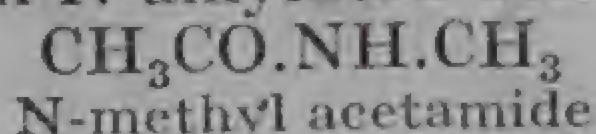
Like acetyl chloride, acetic anhydride is a valuable reagent for introducing acetyl groups into alcohols, phenols, and amines. This process, known as *acetylation*, is carried out as in the case of acetyl chloride (Sec. 185). The reaction with hydroxy compounds is often accelerated by the addition of anhydrous sodium acetate or a little zinc chloride.

III. ACID AMIDES

189. Acid amides, or simply "amides", may be regarded as derived from ammonia by exchanging its hydrogen for acid radicals, when, as in the case of amines, *primary*, *secondary* and *tertiary acid amides* are formed :



The hydrogen of ammonia may be substituted partly by an acid radical and partly by an alkyl group. In such a case the product is termed an N-alkylated acid amide ; *e.g.*,



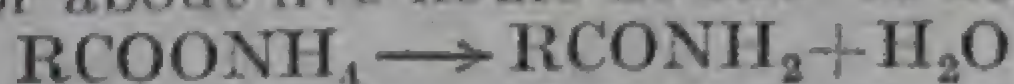
Of the above types, by far the most important are the primary acid amides, commonly known as acid amides, or simply as *amides*.

190. **Preparation.** (1) Amides may be obtained from ammonia by the action of acid chlorides (Sec. 188), acid anhydrides (Sec. 188), or esters. The reaction with acid chlorides is the one usually employed, but where this fails, an ester is used instead of the acid chloride. In this case the reaction occurs as follows :



The ester is shaken with an equal volume of concentrated ammonia until it has dissolved.¹ The mixture is then fractionally distilled. Methyl esters are more readily converted into amides than their higher homologues.

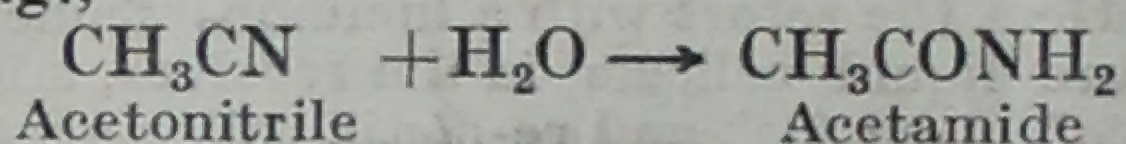
(2) The amide of an acid can also be prepared by slowly distilling it under pressure for about five hours at 220° to 230°.



(3) Finally, they may be obtained from acid nitriles, which take up the elements of water when treated with moderately concentrated

¹ The operation is slow ; in some cases, the mixture may have to stand for several days.

sulphuric acid ; *e.g.*,

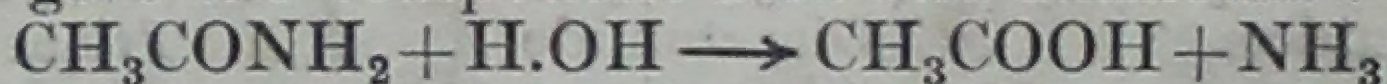


191. Properties. With the exception of formamide, which is a liquid, acid amides are colourless crystalline compounds. The lower members are readily soluble in water and, when pure, are odourless.

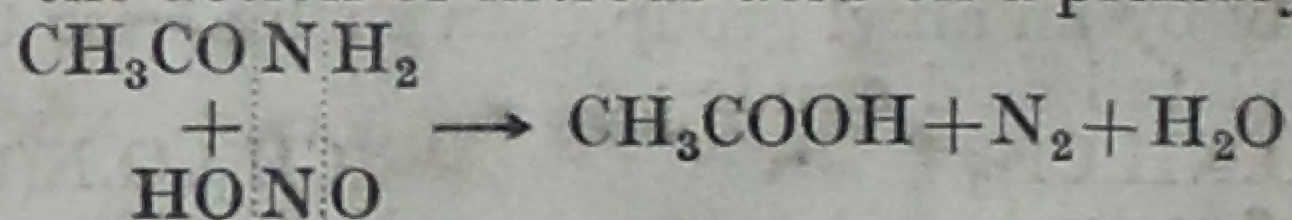
The reactions of amides are as follows :—

(2) The basic character of ammonia having been strongly diminished by the introduction of an acyl group, amides are *neutral* towards litmus. However, they are *amphoteric* in character and possess weakly basic and weakly acidic characters. Thus, when dry hydrogen chloride is passed through an ethereal solution of acetamide hydrochloride, $\text{CH}_3\text{CONH}_2\cdot\text{HCl}$, is formed. On the other hand, hot aqueous solutions of amides dissolve mercuric oxide, forming compounds of the type, $(\text{CH}_3\text{CONH})_2\text{Hg}$.

(2) When heated with alkalies or aqueous mineral acids, amides are hydrolysed to give the component acid and ammonia :



(3) With nitrous acid, the parent acid and free nitrogen are produced (compare the action of nitrous acid on a primary amine) :

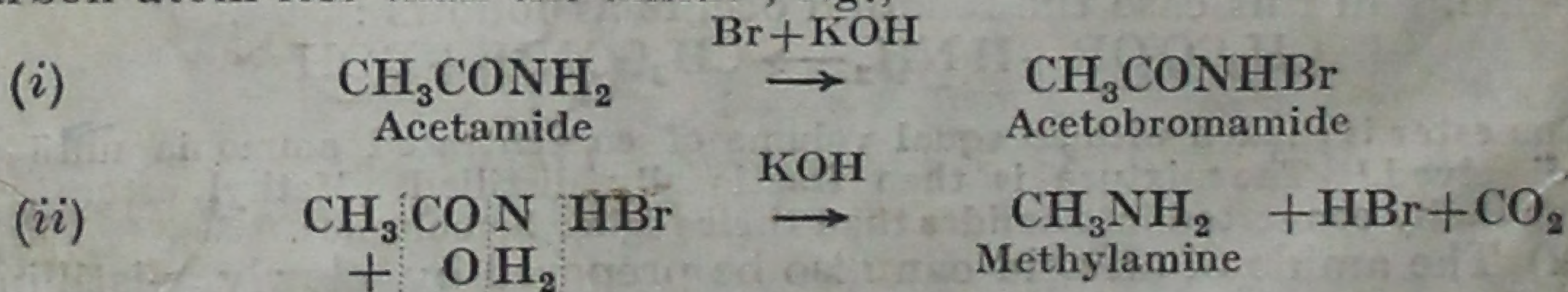


(4) When distilled with phosphorus pentoxide, they yield acid nitriles :



The dehydration can also be effected catalytically (Sec. 66).

(5) **Hofmann's Bromamide Reaction.** When an amide is treated with bromine and aqueous potash, it forms an amine containing one carbon atom less than the amide ; *e.g.*,



The reaction is carried out in two steps :

Step I. The amide (1 mol.) is cautiously mixed with bromine (1 mol.), and a 10 per cent solution of potassium hydroxide (1 mol.) is added, until the colour of bromine has been discharged.

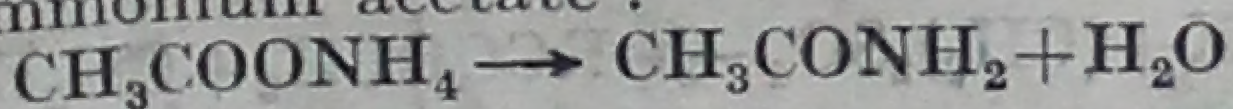
Step II. The reaction product from step I, containing acetobromamide, is added slowly to an excess of a concentrated solution of potassium hydroxide (3 mols).

The reaction may be utilized for descending a homologous series *i.e.* for preparing a lower homologue from a higher one.

(6) *Reaction with Grignard Reagents.* See Sec. 108B.

192. Constitution. The constitution of amides is readily inferred from their formation from ammonia by the action of acid chlorides (Sec. 183). The view is fully supported by the various reactions of these compounds.

193. Acetamide, CH_3CONH_2 . Acetamide is most readily obtained from ammonium acetate:



Ammonium acetate crystals are boiled for 5 to 6 hours with an equal weight of glacial acetic acid under a reflux condenser, the acetic acid acting as a catalyst in the reaction. The product is subjected to fractional distillation (using an air condenser) in order to separate acetamide (b.p. 222°).

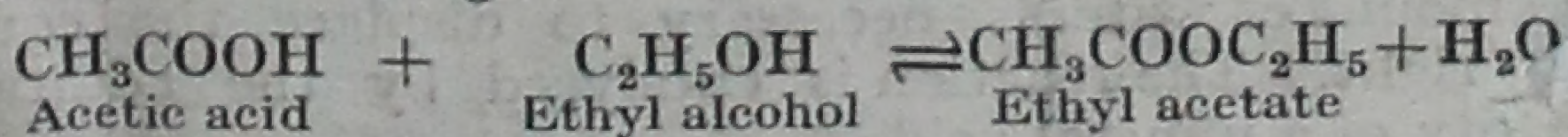
Another very convenient method is by the action of ammonia on ethyl acetate.

Acetamide crystallizes in colourless needles, m.p. 82° and b.p. 222° . It is readily soluble in water and alcohol. Its reactions have already been discussed (Sec. 191.)

IV. ESTERS WITH MONOHYDRIC ALCOHOLS

194. A large number of esters occur in plants, especially in fruits and flowers, which owe their flavour and taste largely to these compounds. In their methods of formation and properties, the esters of monocarboxylic acids are similar to those of the mineral acids (Sec. 127).

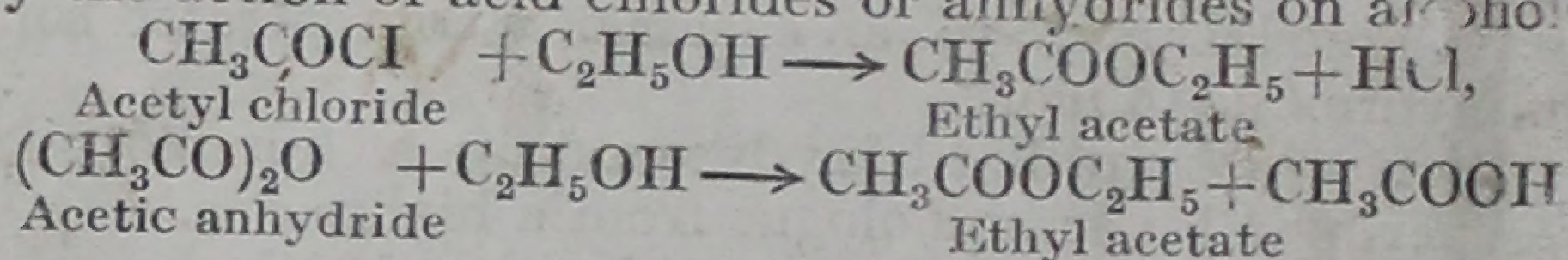
195. Methods of Formation. (1) By the direct interaction of acids and alcohols; *e.g.*,



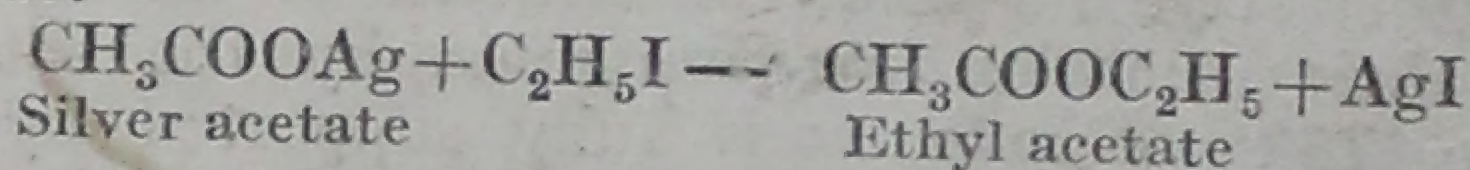
The reaction is reversible, the equilibrium being controlled by the *law of mass action*. In order to reduce the backward hydrolytic action of the water, esterification is carried out in the presence of concentrated sulphuric acid or gaseous hydrogen chloride.

The interaction between alcohols and acids in the vaporous state has been carried out by Sabatier and Maible in the presence of titanium dioxide and thorium dioxide, which act catalytically (Sec. 65).

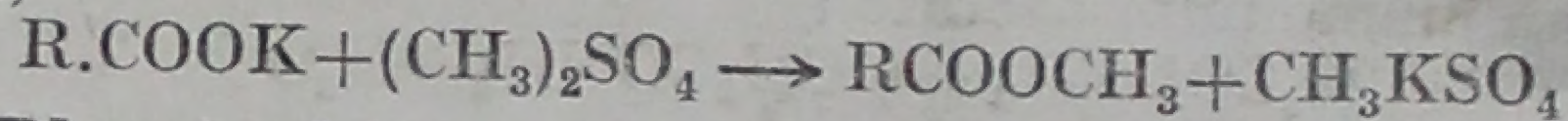
(2) By the action of acid chlorides or anhydrides on alcohols



(3) By double decomposition between the silver salt of the acid and an alkyl halide.



(4) Methyl esters of monocarboxylic acid can be obtained by double decomposition between dimethyl sulphate and potassium salts of the acids ; e.g.,



196. Physical Properties. The lower members are colorless liquids possessing an agreeable

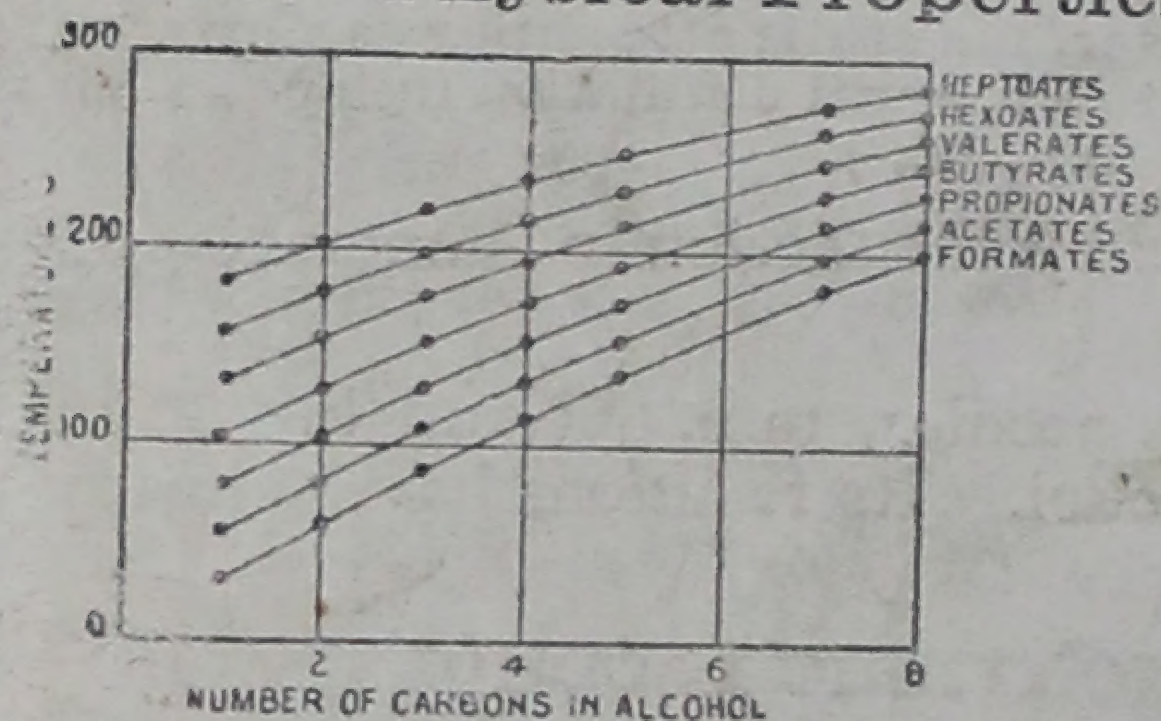


Fig. 77. Boiling points of Esters.

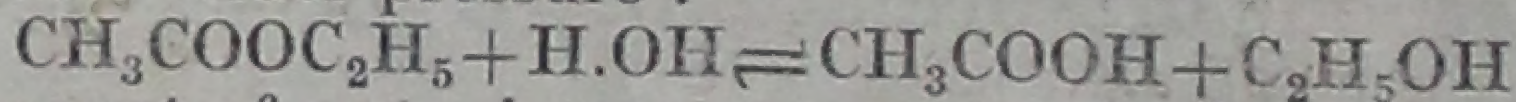
less liquids possessing an agreeable fruity odour. They are generally insoluble in water, but soluble in alcohol and ether.

In Fig. 77 the boiling-points of esters of the normal fatty acids are plotted against the number of carbon atoms in the component alcohols.

197. Reactions. Esters are very reactive substances, and

in most of their reactions the alkoxyl group, —OR, is replaced by other groups. The chief reactions of esters are :

(1) *Hydrolysis.* Hydrolysis or the replacement of —OR by —OH, which is the reversal of esterification, may be effected by heating the ester with water under pressure :



A large amount of water is necessary to displace the equilibrium towards the right. The reaction is catalysed by the addition of a small quantity of a mineral acid.

The hydrolysis of an ester can be carried out *quantitatively* in the presence of an alkali. The latter serves two purposes (i) it acts catalytically, and (ii) it combines with the acid produced thus making the reaction proceed to completion :

